

强化固体氧化物燃料电池阴极耐铬毒化能力的研究进展

朱 峰, 陈 宇

(华南理工大学环境与能源学院, 广州 510006)

摘 要: 固体氧化物燃料电池(SOFCs)是一种极具吸引力的能源转换技术, 具有高效率、低排放、燃料适用性广等优点, 在分布式发电和制氢储能等领域有广泛的应用前景。然而, 在 SOFCs 实际运行工况下, 金属连接体中挥发出来的气态铬物种导致的阴极材料“铬中毒”现象, 是电池性能下降和效率损失的主要原因之一。本文梳理了近年来在提升阴极材料耐铬毒化性能方面的重要进展。首先总结了 SOFCs 阴极材料上铬沉积的相关机制, 而后从多方面详细介绍了缓解阴极材料铬中毒的相关策略。最后, 提出了在强化阴极材料耐铬毒化能力方面所面临的关键挑战及未来可能的研究方向, 以期进一步推进 SOFCs 技术的相关研究和实际应用。

关键词: 固体氧化物燃料电池; 阴极; 铬中毒; 耐铬毒化

中图分类号: TM911.4 文献标志码: A 文章编号: 0454-5648(2025)10-3041-15

网络出版时间: 2025-09-02



能源是人类文明进步的基础和动力。自工业革命以来, 化石能源的大规模利用极大地推动了人类社会的发展, 但也导致了资源枯竭、环境污染和气候变化等一系列问题^[1]。加快推动以高能耗、低效率、高排放的化石燃料为主的能源结构向低碳、高效、可持续的绿色能源转型, 是破解资源环境约束、实现“双碳”目标的迫切需要^[2]。

发展可再生能源是能源结构转型的重要方向。高效、规模化地利用风能、太阳能、氢能等绿色能源, 对现有的能量存储和转换技术提出了新的要求。在各种新型发电与储能技术中, 固体氧化物燃料电池(SOFCs)因其全固态的结构、高的能量转换效率、广泛的燃料适用性, 以及低排放等特点有望成为助力能源绿色低碳转型的重要技术之一^[3-5]。传统的 SOFCs 的工作温度通常在 800 °C 以上^[3, 6]。一方面, 较高的工作温度对 SOFCs 系统各组件材料提出了更高的要求, 尤其是在机械强度、反应性、热膨胀行为及电池密封等方面; 另一方面, 高的工作温度导致了 SOFCs 系统启动时间长、经济竞争力较弱, 这严重阻碍了 SOFCs 技术的商业化进程。将 SOFCs 的运行温度降低到中温范围(600~800 °C), 可以显著

缓解电池各组件之间的化学反应, 延长电池使用寿命, 扩大更廉价材料的选择范围, 提高其经济竞争力^[7-8]。然而, 中温下 SOFCs 的阴极材料对氧还原反应(ORR)的催化活性下降, 导致极化阻抗的快速增加, 电池性能显著下降^[9-10]。因此, 开发在中温下具有优异 ORR 电催化活性和耐久性的阴极材料至关重要^[11]。

在过去的几十年中, 大量的研究工作致力于设计先进的阴极材料^[12-15]。这些材料具有高的电子/离子传导率、优异的电催化活性, 以及与其他电池组件之间良好的化学兼容性和匹配的热膨胀系数。例如, 目前已经商业化的单钙钛矿氧化物 $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$ (LSM) 和 $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ (LSCF)。此外, $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF)、 $\text{Ba}_{1-x}\text{Co}_{0.7}\text{Fe}_{0.2}\text{Nb}_{0.1}\text{O}_{3-\delta}$ (BCFN) 等单钙钛矿材料, $\text{LnBaCo}_2\text{O}_{5+\delta}$ (Ln 为镧系元素) 等双钙钛矿材料及 $\text{La}_2\text{NiO}_{4+\delta}$ 、 $\text{Pr}_2\text{NiO}_{4+\delta}$ 等 Ruddlesden-Popper 类钙钛矿材料也都得到了广泛的研究并且被报道了各自的优势^[16-20]。然而, 尽管研究者们为开发中温下具有高性能和稳定的阴极材料付出了诸多努力并取得了重大进展, 但大多数的阴极的电化学评估都是在相对温和的运行条件下进行

收稿日期: 2025-02-17。 修订日期: 2025-03-12。

基金项目: 国家自然科学基金(22005105)。

第一作者: 朱 峰(1998), 男, 博士研究生。

通信作者: 陈 宇(1985), 男, 博士, 教授。

Received date: 2025-02-17. Revised date: 2025-03-12.

First author: ZHU Feng (1998-), male, Doctoral candidate.

E-mail: zhufeng_x@163.com

Correspondent author: CHEN Yu (1985-), male, Ph.D., Professor.

E-mail: eschenyu@scut.edu.cn

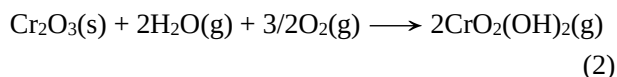
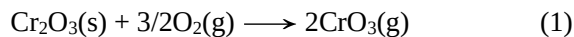
的。而在实际应用中, SOFCs 电堆的阴极不可避免地会遭遇到恶劣的工况条件, 如供应到阴极侧的气体不纯(可能含有水蒸气、CO₂、硫化物等)或者电堆系统组件在高温下挥发出气态污染物[如 CrO₃ 和 CrO₂(OH)₂ 等]。这些污染物会沉积到阴极表面或者直接与阴极发生反应, 从而引起阴极的中毒或者腐蚀现象, 导致严重的性能下降和寿命缩短^[21–23]。其中, 阴极上的“铬中毒”现象是目前广泛关注到的问题之一^[24–25]。与高温环境下使用的陶瓷连接体相比, 中温运行时广泛采用的金属连接体不仅显著降低了成本, 还展现出更高的导电性和导热性, 以及更佳的加工性能^[26]。但是, 金属连接体中通常会添加部分的铬元素来提高其抗氧化和抗腐蚀的能力^[27]。在高温和氧化气氛下, 形成的 Cr₂O₃ 层会挥发出气态的含铬物种[如 CrO₃ 和 CrO₂(OH)₂ 等]。这些气态的含铬物种会和阴极材料表面偏析出来的碱土金属氧化物(如 BaO 和 SrO 等)发生反应, 形成固相沉积物累积到阴极表面^[28]。这些惰性的沉积物不仅会占据阴极上氧反应的活性位点, 导致电催化活性的显著下降, 还可能会影响多孔阴极内的气体扩散, 造成电池的快速衰减。因此, 提升阴极的抗铬毒化能力, 对于维护 SOFCs 系统的稳定性和延长其使用寿命至关重要。

迄今为止, 有许多关于阴极铬毒化的优秀的综述文章被报道^[25, 28–31]。这些综述文章详细地总结了连接体中铬物种的挥发与沉积理论, 阴极材料与铬蒸汽之间的相互作用, 以及缓解阴极材料铬中毒的有效策略。然而, 这些综述重点关注于氧离子传导型固体氧化物燃料电池(O-SOFCs)上传统的 LSM、LSCF 等商业化阴极材料的铬中毒表现和耐铬毒化的措施。相较而言, 本文着重聚焦于强化固体氧化物燃料电池阴极材料耐铬毒化能力的相关研究工作, 不仅探讨了传统阴极材料(如 LSM、LSCF)的掺杂与改性策略, 还涵盖了新型阴极材料的铬中毒现象及其耐铬毒化措施的研究内容。此外, 本文还总结了新兴的质子传导型固体氧化物燃料电池(H-SOFCs)阴极铬中毒的研究工作及该领域面临的重要挑战。本文旨在为耐铬毒化阴极材料的开发提供借鉴与参考, 以期进一步推动 SOFCs 技术的相关研究和实际应用。

1 铬沉积理论

热力学平衡计算表明, 在典型的 SOFCs 工作温度下, 金属连接体中挥发出来的气态铬物种中

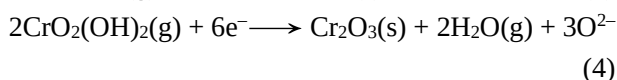
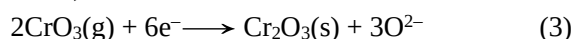
最常见的成分是 CrO₃ 和 CrO₂(OH)₂^[32–34]。这 2 种六价铬物种的相对含量显著依赖于湿空气中 O₂ 和 H₂O 的分压^[35]。此外, 与 CrO₂(OH)₂ 相比, 在 $p(\text{H}_2\text{O})=10\ 132.5\ \text{Pa}$ 和 $p(\text{O}_2)=10\ 132.5\ \text{Pa}$ 的条件下, 温度变化对铬物种中 CrO₃ 分压的影响更为显著。从金属连接体的 Cr₂O₃ 氧化层中挥发出含铬物种的主要反应如下^[35]:



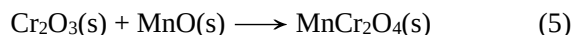
在驱动力的作用下, 这些含铬物种会迁移到阴极表面, 反应形成活性差的铬酸盐, 进而阻碍了阴极的表面氧交换和电子传递, 导致电池性能下降。因此, 深入理解阴极材料在含铬气氛下的铬中毒机制及其影响因素, 对开发耐铬毒化的阴极材料具有重要意义。

1.1 电化学沉积理论

Hilpert 等^[36]基于整个电池反应的过程, 计算了氧还原反应和高氧化态的铬物种[CrO₃ 和 CrO₂(OH)₂]还原反应的吉布斯自由能变化, 结果表明: 气态 Cr 物种的还原驱动力与氧的还原驱动力基本相同, 即高价态的气态 Cr 物种会与 O₂ 竞争活性位点, 这将显著减缓 ORR 的动力学。因此, 在阴极极化电位下, 通过电化学还原形成的固态 Cr₂O₃ 会占据并积累在活性区域, 导致电极的电催化性能迅速下降(图 1a 和图 1b)^[37]。电化学沉积理论的主要反应如下^[37]:



特别地, 对于 LSM 阴极, 在低氧分压或者负的极化的条件下, 沉积的 Cr₂O₃ 还会进一步与 LSM 分解形成的 MnO 发生反应^[38]:



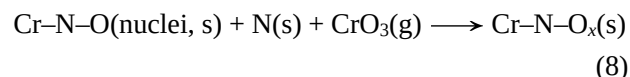
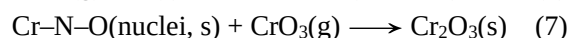
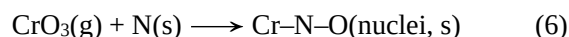
根据电化学沉积理论, 有研究报道高价态的气态 Cr 物种可能会优先沉积在阴极上电子交换活跃的三相界面处^[39–40]。但实际上, 在 Cr 中毒实验中沉积物的分布和组成较为复杂。一方面, 在阴极极化条件下, 不同阴极材料上的 Cr 沉积物的位置和组成都有所区别。例如, 在使用 Fe–Cr 不锈钢连接体及存在阴极极化条件下, Jiang 等^[24, 41]观察到含 Cr 沉积物会优先聚集在 LSM 阴极和氧化钇稳定氧化锆(YSZ)电解质的界面处, 并且在 LSM 阴极边缘形成环状沉积区域。通过能量色散 X 射线谱(EDS)分析得到固态沉积物的主要成分为(Cr,Mn)₃O₄ 尖晶石

相和 Cr_2O_3 相。不同的是, 对于 LSCF 阴极, Cr 沉积物主要以孤立的颗粒分布在阴极的表面, 且主要成分为 SrCrO_4 相^[24]。另一方面, 极化电流在 Cr 沉积中也起着重要的作用。Taniguchi 等^[42]比较了 LSM 阴极在开路 and 恒定电流($300 \text{ mA} \cdot \text{cm}^{-2}$)这 2 个条件下的极化损失和 Cr 沉积物的含量。结果表明, 施加阴极极化电流之后, Cr 沉积物积累量会显著增加。值得注意的是, 有文献报道在开路和阳极极化的条件下也观察到了 Cr 沉积现象^[41, 43]。然而, 在这 2 种条件下, 气态的 Cr 物种无法被还原。因此, 电化学沉积理论可能无法解释这些情况下的铬中毒现象。

1.2 化学沉积理论

Jiang 等^[41, 44-46]系统地研究了常见的几种阴极材料的铬中毒现象, 并且提出了化学沉积理论(图 1c

和图 1d)。即阴极材料中偏析出来的金属离子作为成核剂与连接体中 Cr_2O_3 层挥发出来的气态 Cr 物种发生了成核反应。主要反应如下:



其中: N 表示阴极材料中偏析出来的成核剂(如 Mn^{2+} 、 Sr^{2+} 、 Ba^{2+} 等); Cr-N-O_x 表示所形成的 Cr 沉积物[如 $(\text{Cr}, \text{Mn})_3\text{O}_4$ 、 SrCrO_4 、 BaCrO_4 等]。显然, 根据这一理论, Cr 沉积物的组成和分布本质上取决于阴极上的偏析的成核剂的分布^[47]。此外, 值得注意的是, LSM 阴极中高价态的 Mn 元素的电化学还原是 Mn^{2+} 的主要来源。

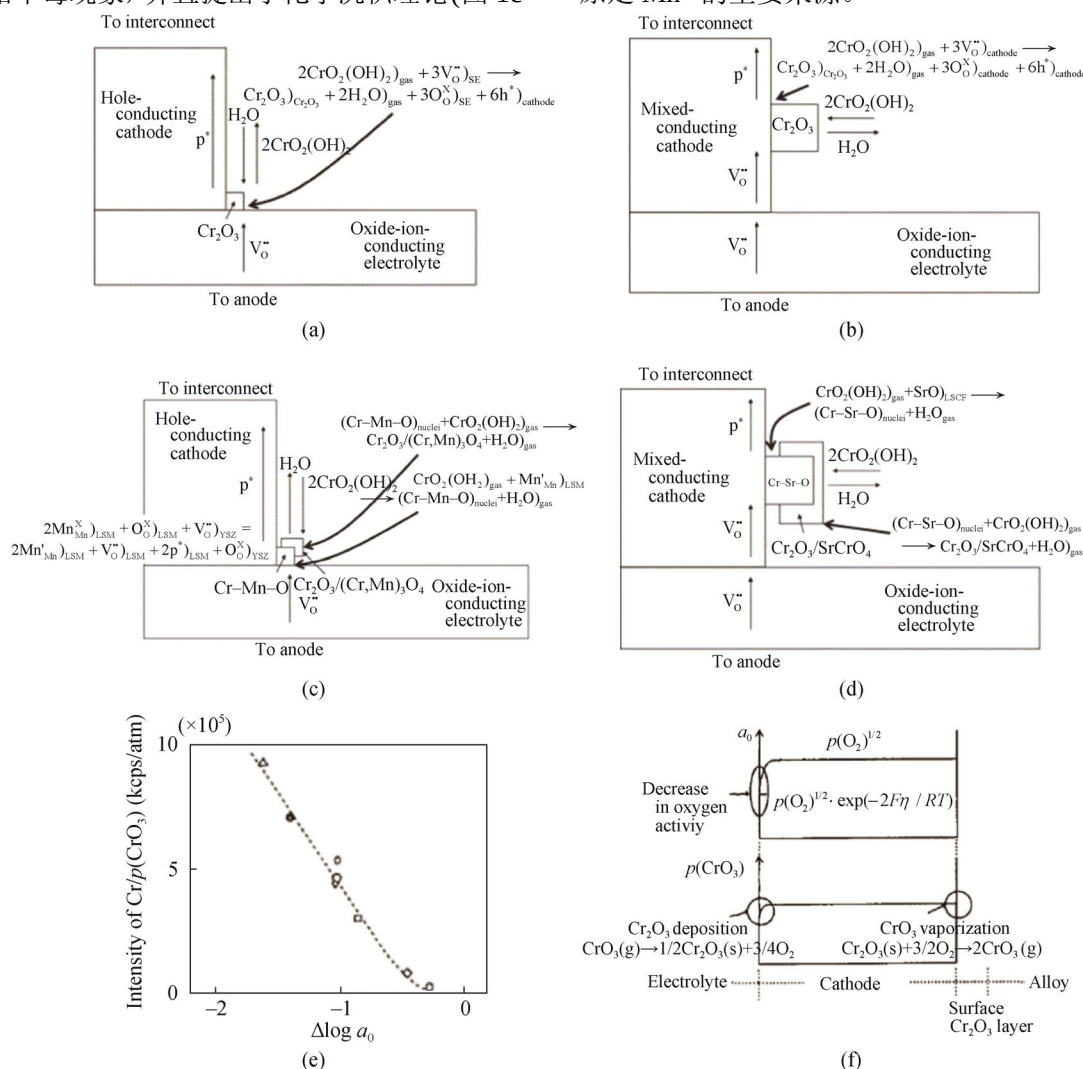
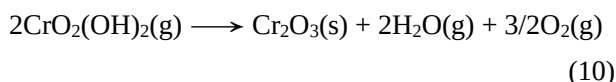
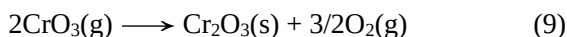


图 1 (a)空穴传导的阴极和(b)混合传导的阴极的电化学沉积示意图^[48]; (c)空穴传导的阴极和(d)混合传导的阴极的化学沉积示意图^[48]; (e)阴极/电解质界面处 Cr 的强度与计算的 CrO_3 蒸汽压的比值和界面处相较于气相降低的氧活度之间的关系^[42]; (f)氧活度理论示意图^[42]

Fig. 1 Schematics of electrochemical deposition of (a) hole-conducting cathode and (b) mixed-conducting cathode^[48]; Schematics of chemical deposition of (c) hole-conducting cathode and (d) mixed-conducting cathode^[48]; (e) Relationship between the ratio of the intensity of Cr at the cathode/electrolyte interface to the calculated CrO_3 vapor pressure and the decrease in oxygen activity at the interface from the gas phase; (f) Schematics of oxygen activity theory^[42]

1.3 氧活度理论

Taniguchi 等^[42]认为在 LSM 阴极和电解质界面处形成的 Cr 沉积物是由于氧活度的下降而导致的。电池放电时, 阴极侧的氧气被连续的消耗, 界面处的低氧分压促进了以下的反应:



Taniguchi 等用式(11)定义了氧活度 a_{O_2} :

$$a_{\text{O}_2} = p(\text{O}_2)^{\frac{1}{2}} \times \exp(-2\eta F/RT) \quad (11)$$

其中: $p(\text{O}_2)$ 为阴极气体中的氧分压; η 为电池测试时起始的阴极极化; F 、 R 和 T 分别为法拉第常数、气体常数和温度。因此, 阴极/电解质界面处相对于阴极的气相中, 降低的氧活度为 $\Delta \log a_{\text{O}_2} = -(2\eta F/RT) \lg e$ ^[42]。结果表明, 阴极/电解质界面处 Cr 的强度与计算的 CrO_3 蒸汽压的比值和 $\Delta \log a_{\text{O}_2}$ 密切相关, 如图 1e 所示。因此, 阴极/电解质界面处的 Cr 累积是由于电池放电时界面处的氧活度下降所引起的(图 1f)。Yokokawa 等^[49]进行的热力学分析结果也支持了这一理论, 在极化条件下 Cr 沉积量的增加是由于发生 ORR 反应时阴极层中存在氧电势梯度所导致的。

2 提升阴极材料耐铬毒化的措施

当前的研究主要从以下 3 个方面来强化阴极材料的耐铬毒化的能力: 1) 在源头上抑制金属连接体中铬蒸汽的挥发, 如优化金属连接体的组成、为金属连接体添加表面涂层; 2) 阻断气态铬物种向阴极材料的扩散, 如添加铬蒸汽吸收剂; 3) 优化阴极材料的组成和结构来抑制元素的偏析或富集, 如表面修饰、元素掺杂等。

2.1 从源头上抑制铬蒸汽的产生

降低金属连接体中的 Cr 元素含量或添加其他元素来改变表面氧化相的组成和微观结构, 是缓解阴极材料铬中毒的有效方式之一。Chen 等^[50]报道了一种新型的 Ni–Mo–Cr 合金连接体。该合金连接体中的 Cr 元素含量几乎是 RA446 Fe–Cr 合金连接体的一半, 并且额外添加了 Mo、Ni 等元素。对 Ni–Mo–Cr 合金连接体的表面氧化层的相分析表明, 在合金外部的 Cr_2O_3 层之上还形成了一层 NiMn_2O_4 尖晶石相。表面不含 Cr 的 NiMn_2O_4 层的形成显著减少了 Cr 元素向表面的扩散及铬物种的挥发。相似地, Zhang 等^[51]开发了低 Cr 含量的 Fe–Cr–Co 合金用作

中温 SOFCs 的连接体。在工作温度下, Cr_2O_3 外部形成的致密的 $(\text{Mn}, \text{Cr})_3\text{O}_4$ 外层有效地抑制了 Cr 物种的挥发。需要注意的是, 开发新型的合金连接体材料可能需要较高的成本。此外, 电堆系统的附属管道、阀门等也存在 Cr 蒸汽的挥发。

用于连接体的表面保护性涂层材料应该满足以下要求: 高的导电率、合适的热膨胀系数, 以及能够阻止阳离子的向外迁移和氧气的向内扩散。当前, 研究者报道了多种类型的表面涂层可以有效抑制连接体中的 Cr 物种的挥发, 主要包括钙钛矿(如 LaCrO_3 、 $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$) 和尖晶石[如 $(\text{Mn}, \text{Co})_3\text{O}_4$ 、 CuFe_2O_4 等]结构的表面涂层^[52–53]。由于具有足够的电导率, 并且与电池组件具有匹配的热膨胀系数和良好的化学相容性, LSM 也被用作连接体的涂层材料^[54–55]。Palcut 等^[54]通过等离子喷涂将单层的 LSM 沉积到商用连接体的表面来研究其的高温氧化行为。结果表明, LSM 可以作为氧的传输屏障, 并且降低了涂层与氧化铬界面处的氧分压。然而, 将 LSM 涂层包覆的 Crofer 22 APU 在 1123 K 和 O_2 下氧化 1000 h 后, 能量色散 X 射线光谱(EDS)分析中仍然观察到了一定的 O^{2-} 和 Cr^{3+} 扩散。Lenka 等^[56]通过丝网印刷将 $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_3$ (LSCM) 用作铁素体不锈钢的保护涂层。在 800 °C 下暴露于空气中 300 h 后, 涂有 LSCM 涂层的铁素体不锈钢的面积比电阻低至 $2.0 \text{ m}\Omega \cdot \text{cm}^2$ 。X 射线衍射(XRD)及 EDS 分析进一步表明, 在富 Cr 氧化层之上形成的 $(\text{Mn}, \text{Cr})_3\text{O}_4$ 层是抑制 Cr 物种扩散的主要原因。Molin 等^[55]比较了通过电泳沉积、热蒸发和磁控溅射 3 种方法在 Crofer 22 APU 基体表面制备的 $(\text{Mn}, \text{Co})_3\text{O}_4$ 尖晶石涂层的面积比电阻。结果表明, 在 800 °C, $0.5 \text{ A} \cdot \text{cm}^{-2}$ 的条件下氧化 5000 h, 通过电泳沉积制备的尖晶石涂层实现了最低的面积比电阻和最低的阻抗值增长率。而通过热蒸发和磁控溅射制备的尖晶石涂层在 Cr 保留能力和抑制氧化铬层生长等方面的有效性不如电泳沉积的方式。此外, Zhao 等^[57]开发了一种纳米尺寸的球形 CuFe_2O_4 尖晶石粉末作为涂层材料(图 2a)。其因优异的烧结能力, 可以不经额外的热处理而直接应用于 SOFCs。在 800 °C, 0.8 V 的恒电位下运行, 使用添加 CuFe_2O_4 涂层的 SUS430 不锈钢连接体时, 单电池在 100 h 的衰减速率仅为 6.7%。而不含涂层时, 单电池的衰减速率达到了 81% (图 2b 和图 2c)。Zhao 等^[58]采用磁控溅射技术在 SUS430 不锈钢基体上制备一种 NiFe_2 合金涂层。在 800 °C 的空气中暴露 15 周

后, 观察到在氧化铬亚层之上形成了 NiFe_2O_4 尖晶石层, 从而达到了抑制 Cr 挥发的效果。

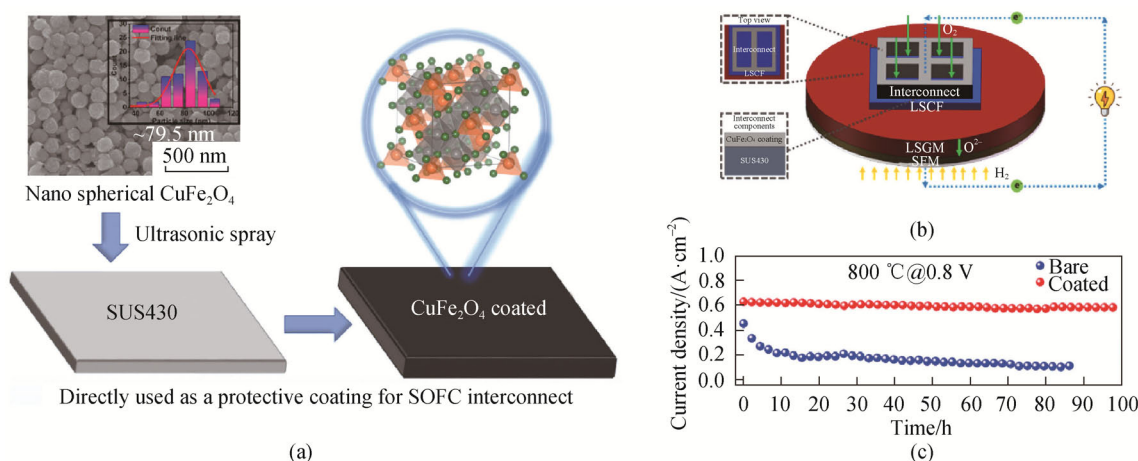


图 2 (a) CuFe_2O_4 尖晶石涂层包覆的 SUS430 连接体示意图^[57]; (b) 用于测试的电池结构和互联的示意图^[57]; (c) 单电池在 800 °C, 0.8 V 的恒电位下的运行 100 h 的稳定性^[57]

Fig. 2 (a) Schematic of CuFe_2O_4 spinel coated SUS430^[57]; (b) Schematic of the cell structure and interconnection during the cell test^[57]; (c) Stability test for single cells operated at 800 °C for 100 h under a potentiostat of 0.8 V^[57]

2.2 阻断铬蒸汽的扩散

铬吸收剂通常被放置在阴极侧的空气入口处, 以在 Cr 蒸汽到达阴极之前降低其分压。SrO 被认为是铬吸收剂有效成分, 可以捕获挥发出来的气态铬物种, 进而形成热力学上稳定的固相 SrCrO_4 ^[59]。然而, SrO 容易形成氢氧化物和碳酸盐, 这将导致体积膨胀及吸气层与支撑基底的分离^[60]。因此, 铬吸收剂通常由 SrO 与过渡金属氧化物复合制成, 如 $\text{Sr}_x\text{Ni}_y\text{O}_z$ (SNO) 和 SrMnO_3 等。Uddin 等^[61]比较了外置和内置 SNO 铬吸收剂时对电池稳定性的影响(图 3a 和图 3b)。考虑到内置铬吸收层时对电导率的不利影响, 研究者将 SNO 与不同比例的 LSCF 进行了混合, 以尽可能消除对电化学测试的影响。如图 3c 所示, 将没有放置铬源和铬吸收剂的半电池性能作为基线, 外置铬吸收剂的半电池(Config-1)几乎没有表现出性能的下降; 内置 75% LSCF-25% SNO 层的半电池(Config-2)表现出接近基线的性能。而内置 50% LSCF-50% SNO 层的半电池(Config-2)性能略差, 这可能是由于 SNO 具有相对较低的电导率。Heo 等^[60]将 SNO 铬吸收剂安装于电池前方的空气入口处(图 3d), 来探究铬吸收剂在中温(550~650 °C)下捕获铬物种的效果。无论在 650 °C 还是 550 °C 的 100 h 稳定性测试中, 半电池均表现与基线相近的稳定性, 进而证实了 SNO 铬吸收剂在中温下的有效性(图 3e 和图 3f)。此外, 铬吸收剂在长期使用过程中会不断被消耗, 需要及时补充或者更换。

2.3 优化阴极材料的组成和结构

2.3.1 阴极材料的表面修饰

大量的研究表明, 通过对阴极材料进行表面修饰来强化其抗铬毒化能力是一种有效的策略^[10, 31, 59, 62]。Zhao 等^[63]探究了钐掺杂的氧化铈(GDC)浸渍的 LSCF 电极在使用 RA446 (23%~27% Cr)连接体时的电化学表现。结果表明, 浸渍的 GDC 纳米颗粒显著降低了 LSCF 阴极上 ORR 的活化能。同时, GDC 作为阻挡层提高了 LSCF 阴极对 Cr 污染的耐受性。进一步, Han 等^[64]报道了一种基于 CeO_2 开发的高熵催化剂 ($\text{La}_{0.2}\text{Pr}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Gd}_{0.2}\text{O}_{2-\delta}$ (HEDC))。相较于未浸渍的 LSCF、GDC 浸渍的 LSCF 及钐掺杂的氧化铈(SDC)浸渍的 LSCF, HEDC 浸渍的 LSCF 阴极的催化活性和 Cr 耐受性显著提高。在 800 °C 的含铬气氛下处理 100 h, HEDC-LSCF 的极化阻衰减速率显著低于 LSCF、GDC-LSCF 和 SDC-LSCF。

浸渍含钡化合物[如 BaO , BaCO_3 , BaCoO_{3-x} (BCO)等]同样可以在提升阴极电催化活性的同时, 强化阴极的耐铬毒化能力。Chen 等^[65]将 BaO 浸渍到 LSCF 阴极表面, 显著减少了 LSCF 的表面 Sr 偏析并缓解了铬中毒造成的不良影响。研究者认为浸渍的 BaO 纳米颗粒会优先与 Cr 物种反应, 在表面形成相对导电的且热力学上更稳定的 BaCrO_4 (800 °C 下的电导率为 $4.5 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$), 进而抑制了惰性的 SrCrO_4 (800 °C 下的电导率为 $1.8 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$) 生成^[66]。相似地, Huang 等^[67]通过表面浸渍 BaCO_3

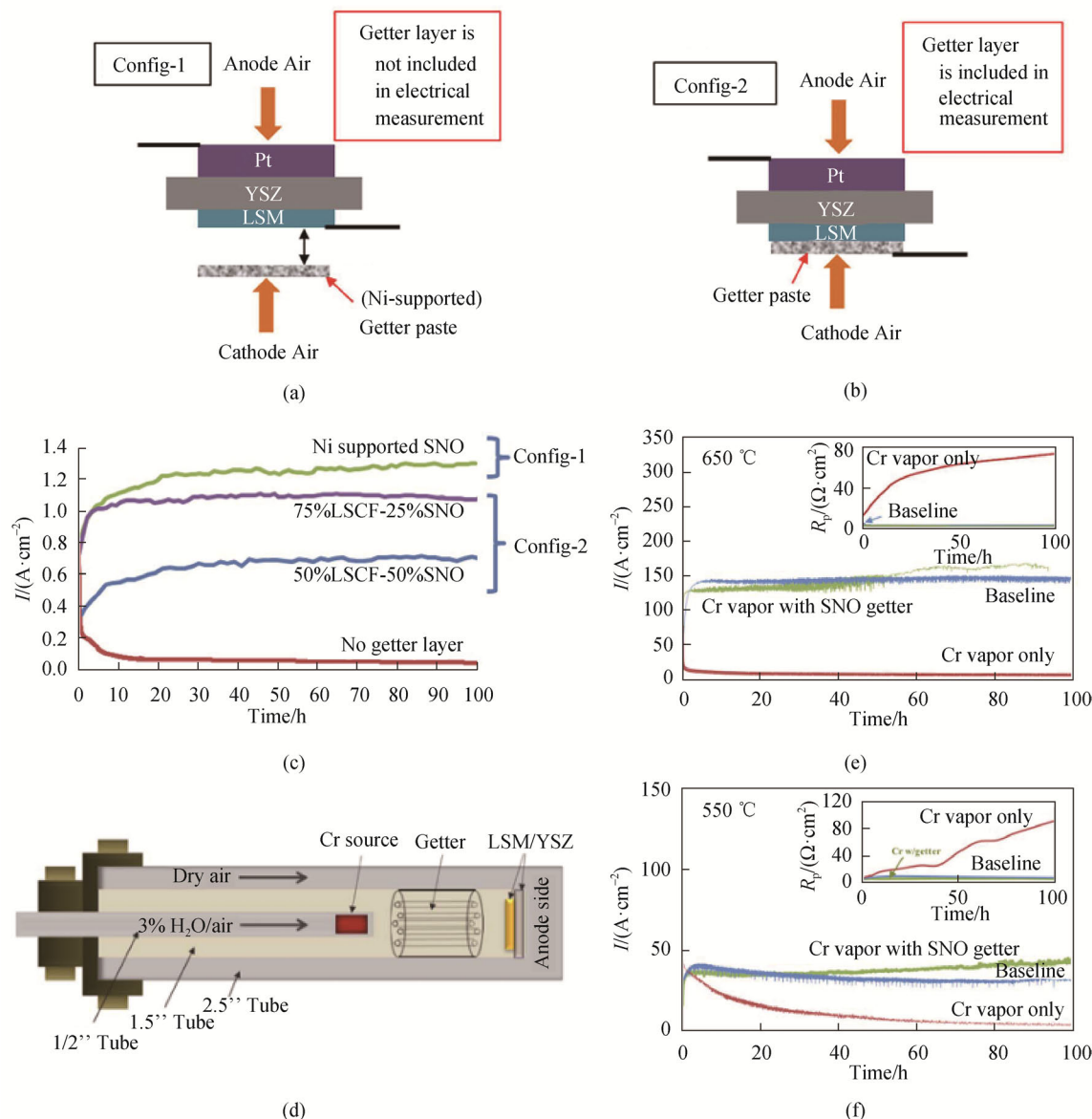


图3 验证铬吸收剂效果的实验装置: (a)配置-1, 吸收剂材料涂覆在 Ni 网上, 并放置在距离 LSM 阴极 5 mm 的位置^[61]; (b) 配置-2, 吸收剂材料涂覆在 LSM 阴极上^[61]; (c)应用吸收剂配置-1、吸气剂配置-2 和不具有吸收剂层时, 测试半电池在 0.5 V 偏压下的性能(在 850 °C 下测试电池, Cr_2O_3 粉末作为铬源^[61]); (d)存在铬源和铬吸收剂时, 半电池的电化学测试装置示意图^[60]; 在(e) 650 °C 和(f) 550 °C 下测试的 3 个半电池的电-时间曲线(内置图为相应的极化阻抗-时间曲线)^[60]

Fig. 3 Experimental setup for the validation of Cr getter: (a) config-1: getter material is coated on Ni Mesh and placed 5 mm away from LSM cathode^[61]; (b) config-2: getter material is coated on LSM cathode^[61]; (c) Half-cell performances measured at 0.5 V bias when cells were tested with getter config-1, getter config-2, and no getter layer (the cells were tested at 850 °C with Cr_2O_3 powder as the Cr source^[61]); (d) Schematic of the electrochemical test setup for the half-cell in the presence of Cr source and Cr getter^[60]; I - t curves of the three half-cells tested at (e) 650 °C and (f) 550 °C (the insets are the corresponding polarization R_p - t curves)^[60]

来强化 LSCF 阴极的抗 Cr 中毒能力, 并提出了相关的机制(图 4a)。处于连接体腔道下(间接接触)的阴极表面 Cr 沉积物的含量显著下降, 这主要是归因于 BaCO_3 与气态 CrO_3 之间具有较高的反应能垒; 而对于在连接体肋部下(直接接触)的阴极区域, BaCO_3 会优先与 Cr_2O_3 反应形成 BaCrO_4 层, 从而达到抑制 LSCF 表面 SrO 的偏析和 SrCrO_4 的形成。正是由于

这种协同作用使得 BaCO_3 浸渍的 LSCF 阴极具有出色的铬耐受性。Pei 等^[68]提出 BCO 催化剂可以显著提高 LSCF 阴极的 ORR 活性和稳定性, 如图 4b 所示。在 700 °C 下与 Crofer 22APU 直接接触, 作为对照组的使用 LSCF 阴极的单电池的最大功率密度为 $\sim 0.448 \text{ W} \cdot \text{cm}^{-2}$, 在 0.8V 的恒电位测试中衰减速率为 $0.31\% \text{ h}^{-1}$; 而采用 BCO 修饰的 LSCF 阴极的单

电池的最大功率密度为 $\sim 0.514 \text{ W} \cdot \text{cm}^{-2}$, 相应的衰减速率仅为 $0.086\% \text{ h}^{-1}$ (图 4c 和图 4d)。

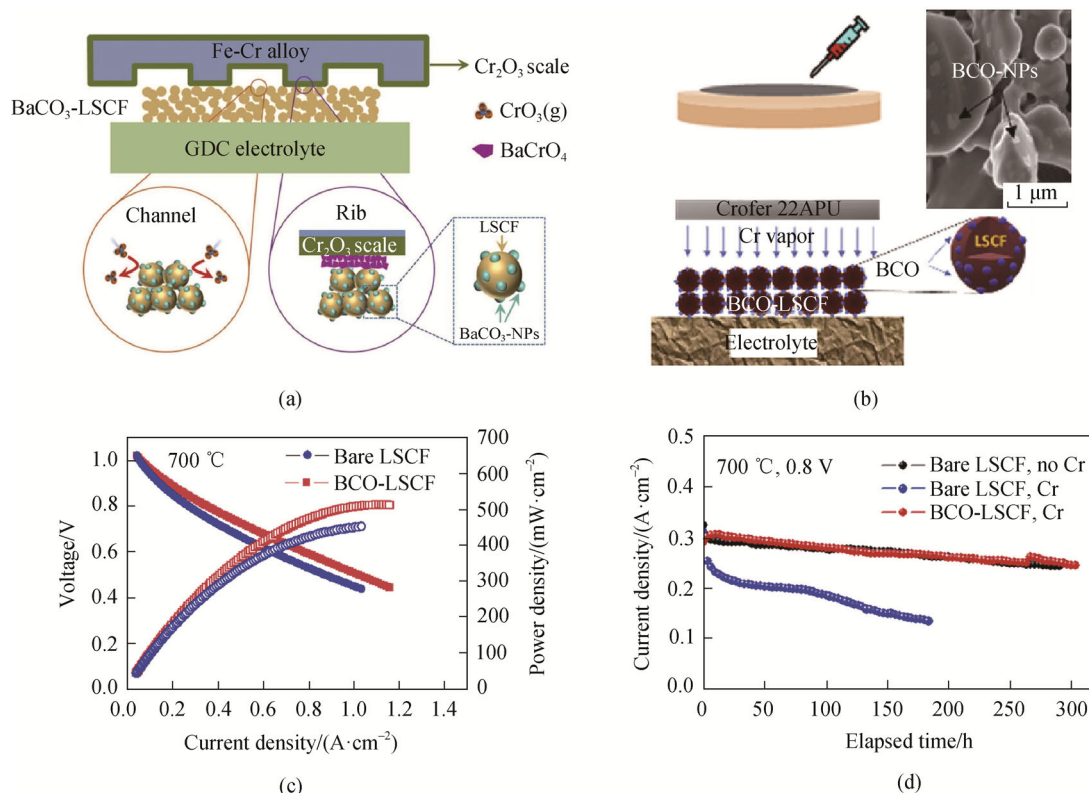


图 4 (a) BaCO_3 浸渍的 LSCF 阴极抗铬毒化的机制^[67]; (b) 铬中毒测试中采用 BCO-LSCF 阴极的对称电池示意图^[68]; (c) 在 700 °C 与 Crofer 22APU 直接接触时, 采用 LSCF 或 BCO-LSCF 阴极的电池的电流-电压-功率曲线^[68]; (d) 对在清洁空气中的 LSCF 阴极, 在 3% H_2O 加湿空气中与铬直接接触的 LSCF, BCO-LSCF 进行的单电池耐久性测试^[68]

Fig. 4 (a) Mechanism of resistance to Cr poisoning of BaCO_3 impregnated LSCF cathode^[67]; (b) Schematics of symmetrical cells with BCO-LSCF cathode for Cr-poisoning test^[68]; (c) I - V - P curves of the cells with a bare LSCF or BCO-LSCF cathode at 700 °C in direct contact with Crofer 22APU^[68]; (d) Durability tests of single cells with bare LSCF cathode in clean air, bare LSCF, and BCO-LSCF in 3% H_2O humidified air and a direct Cr contact^[68]

近年来, 多相催化剂涂层/纳米颗粒在提升阴极材料抗铬中毒能力方面表现出显著效果^[69-71]。如图 5 所示, Chen 等^[69]使用拉曼光谱评估了铬蒸汽与使用不同的表面催化剂改性的 LSCF 电极之间的反应性。该研究中评估的一系列无 Sr 催化剂, 如 $\text{La}_{0.8}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ 、 $\text{La}_{0.8}\text{Ca}_{0.2}\text{Ni}_{0.4}\text{Fe}_{0.6}\text{O}_{3-\delta}$ 、 BaO 、 $\text{Pr}_{0.75}\text{Ca}_{0.2}\text{MnO}_{3-\delta}$ 、 $\text{Pr}_{0.8}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ 及 $\text{PrNi}_{0.5}\text{Mn}_{0.5}\text{O}_3$ (PNM)+ PrO_x 混合催化剂, 均通过相同的方式一步浸渍到 LSCF 阴极上。通过将多孔阴极直接与 Crofer 22APU 接触, 并在 750 °C 且含 3% H_2O 的气氛下退火 75 h 来模拟铬中毒过程。结果表明, PNM+ PrO_x 的混合催化剂修饰的 LSCF 阴极检测出最小的 CrO_4^{2-} 拉曼峰强(图 5a 和图 5b)。随后, 研究者在对称电池上进一步对比了混合催化剂修饰的 LSCF 阴极和未修饰 LSCF 阴极的电化学性能。混合催化剂涂层修饰的 LSCF 阴极表现出更小的初始极化阻抗值和更优异的极化阻抗稳定性(图 5c 和

图 5d)。进一步的表征分析显示, 混合催化剂在 LSCF 表面形成了均匀致密的 PNM 涂层和 PrO_x 纳米颗粒(图 5a)。其中, PNM 涂层可以有效地抑制 LSCF 中 SrO 的偏析, PrO_x 纳米颗粒则可以提供额外的 ORR 活性位点, 两者协同使得修饰后的 LSCF 阴极具有更优异的催化活性和抗铬毒化能力。相似地, Niu 等^[71]构建了一种由 BCFN 和 BaCO_3 组成的多相催化剂涂层来提高 LSCF 阴极在空气气氛下和含铬污染气氛下的 ORR 活性和稳定性。在加速铬中毒实验中(750 °C), 该催化剂修饰的 LSCF 电极在 200 h 测试中的衰减速率为 $10^{-3} \Omega \cdot \text{cm}^2 \cdot \text{h}^{-1}$ ($0.59\% \text{ h}^{-1}$), 仅为对照组空白 LSCF 阴极衰减速率的五分之一。基于密度泛函理论的计算表明: 表面的 BCFN 相提高了 LSCF 阴极的 ORR 活性, 而 BaCO_3 相则强化了 LSCF 阴极的稳定性。表 1 中比较了应用催化剂修饰的 LSCF 阴极的 O-SOFCs 在含 Cr 气氛下的衰减速率。

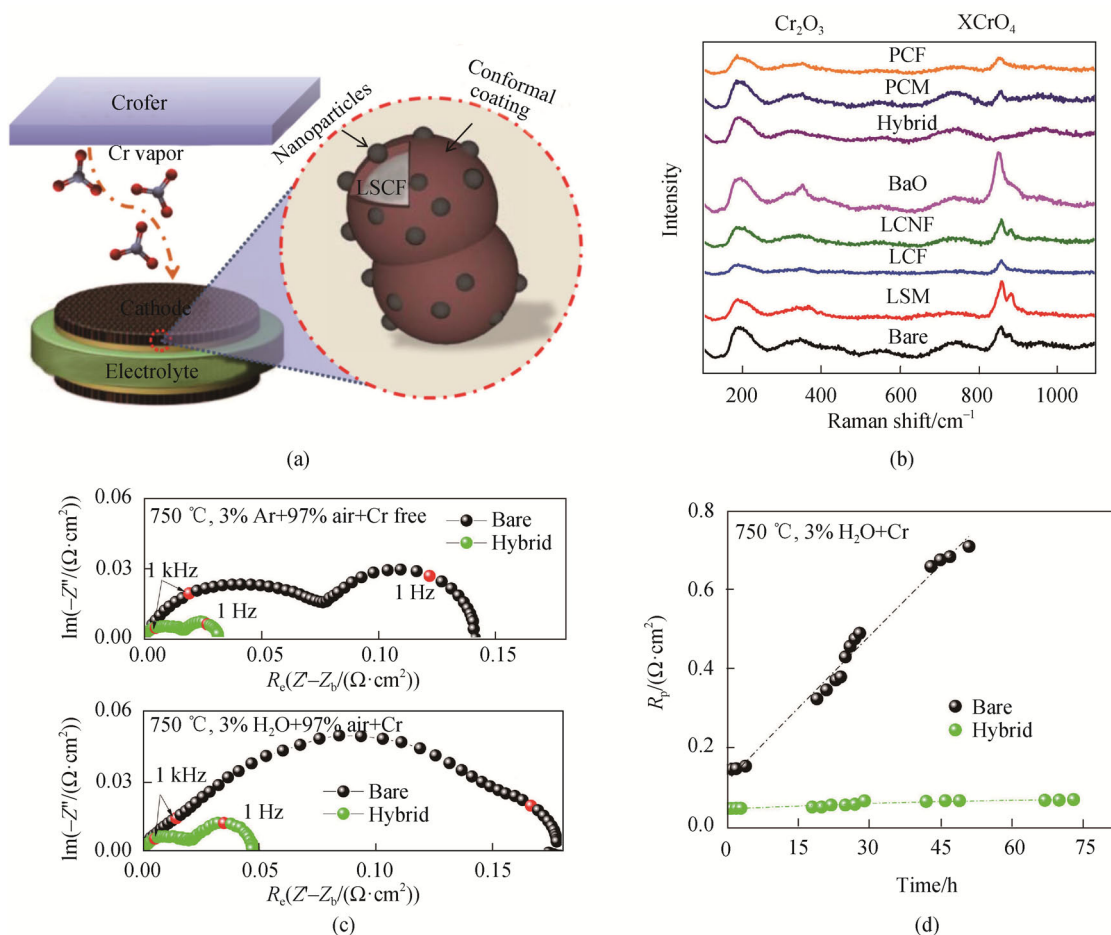


图 5 (a)具有铬容忍性和 ORR 活性的混合催化剂涂层的 LSCF 阴极示意图^[69]; (b)在 750 °C 且含有 3% H_2O 的空气中退火 75 h 后, LSCF 和不同催化剂涂覆的 LSCF 的拉曼光谱^[69]; (c)在 750 °C 的开路电压下, 在清洁空气(3% Ar+97% 空气+无 Cr)和含 Cr 的空气(3% H_2O +97% 空气+直接 Cr 接触)中测试的 LSCF 和混合催化剂涂覆的 LSCF 的电化学阻抗谱(测试开始时)^[69]; (d)在含铬污染条件下, LSCF 和混合催化剂浸渍的 LSCF 的极化阻抗稳定性^[69]

Fig. 5 (a) A schematics of a LSCF cathode coated with a hybrid catalyst coating with Cr tolerance and ORR activity^[69]; (b) Raman spectra of bare LSCF and catalysts coated LSCF annealed under the condition of 750 °C for 75 h with air containing 3% H_2O ^[69]; (c) Electrochemical impedance spectroscopy (at the beginning of the test) of bare LSCF and hybrid catalyst-coated LSCF in symmetrical cells measured at 750 °C under open circuit voltage conditions in clean air (3% Ar+97% air+Cr free) and air with Cr (3% H_2O +97% air+ direct Cr contact)^[69]; (d) R_p stabilities of LSCF and hybrid catalyst-coated LSCF cathodes under conditions of Cr contamination^[69]

表 1 在 Cr 污染条件下, 应用催化剂修饰的 LSCF 阴极的 O-SOFCs 衰减速率对比

Table 1 Comparison of the O-SOFCs degradation rates of the cells with catalyst-decorated LSCF cathodes under Cr contamination conditions

Catalysts coating	Cathode	$T/^\circ\text{C}$	Load	Operating conditions	Degradation rates/ h^{-1}		Ref.
					Bare	Coated	
$\text{PrNi}_{0.5}\text{Mn}_{0.5}\text{O}_3 + \text{PrO}_x$	LSCF	750	0.7 V	3% H_2O +Cr+air	0.40%	0.043 4%	[69]
BaCoO_{3-x}	LSCF	700	0.8 V	3% H_2O +Cr+air	0.31%	0.056 0%	[68]
$\text{Ba}_{1-x}\text{Co}_{0.7}\text{Fe}_{0.2}\text{Nb}_{0.1}\text{O}_{3-\delta} + \text{BaCO}_3$	LSCF	650	$250 \text{ mA} \cdot \text{cm}^{-2}$	3% H_2O +Cr+air	0.13%	0.050 0%	[71]
$\text{Gd}_{0.1}\text{Pr}_{0.1}\text{Ce}_{0.8}\text{O}_{2-\delta}$	LSCF	700	$500 \text{ mA} \cdot \text{cm}^{-2}$	3% H_2O +Cr+air	0.29%	0.006 0%	[62]
$\text{Ba}_{1-x}\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{3-\delta} + \text{BaCO}_3$	LSCF	750	$200 \text{ mA} \cdot \text{cm}^{-2}$	Cr+air	0.18%	0.030 0%	[70]
$(\text{La}_{0.2}\text{Pr}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Gd}_{0.2})_{0.2}\text{Ce}_{0.8}\text{O}_{2-\delta}$	LSCF	750	$500 \text{ mA} \cdot \text{cm}^{-2}$	Cr+air	0.20%	0.110 0%	[64]

当前, 通过表面修饰来提高阴极材料的铬容忍性的研究工作主要集中于 O-SOFCs。由于相对较高

的工作温度加剧了连接体中气态铬物种的挥发, O-SOFCs 的阴极通常会面临严重的铬中毒问题。然

而,对 H-SOFCs 上的铬中毒问题的研究工作相对较少。虽然其相对较低的运行温度使得连接体中挥发的铬蒸汽含量有所下降,但是 H-SOFCs 在阴极侧会有 H_2O 的产生(电池模式)或者消耗(电解模式),这可能会进一步加剧阴极中 BaO 和 SrO 等物种的偏析或富集^[72-73]。因此,在开发适用于 H-SOFCs 的阴极材料时,考察其抗铬毒化的能力是非常必要的。考虑到 H-SOFCs 中典型的阴极材料 $\text{PrBa}_{0.5}\text{Sr}_{0.5}\text{Co}_{1.5}\text{Fe}_{0.5}\text{O}_{5+\delta}$ (PBSCF) 中碱土金属元素的偏析问题,Zhang 等^[74]通过在 PBSCF 上浸渍 $\text{Pr}_{0.9}\text{Fe}_{0.7}\text{Co}_{0.3}\text{O}_3$ (PFC) 催化剂来强化其在 H-SOFCs 上的 ORR 活性及污染物中毒容忍性,在存在铬污染和 3% H_2O 的运行气氛下,采用 PFC-PBSCF 阴极的单电池在 650 °C 下最大功率密度为 $1.08 \text{ W}\cdot\text{cm}^{-2}$,稳定性测试中的衰减速率为 $0.03\% \text{ h}^{-1}$,远优于使用 PBSCF 阴极的单电池(最大功率密度为 $0.75 \text{ W}\cdot\text{cm}^{-2}$,稳定性测试中的衰减速率为 $0.12\% \text{ h}^{-1}$)。拉曼光谱测试表明,PFC 催化剂能够有效地减少 PBSCF 表面上的 Cr 沉积物的积累量。

2.3.2 新型耐铬中毒的阴极材料的开发 尽管在含 Ba 的阴极材料上也会发生 Cr 沉积,但 Cr 沉积物 BaCrO_4 对阴极材料的影响要低于 SrCrO_4 和 $(\text{Mn,Cr})_3\text{O}_4$ ^[75]。Chen 等^[76]系统的研究了不同比例的 Ba 代替 Sr 时, $\text{La}_{0.6}\text{Sr}_{0.4-x}\text{Ba}_x\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSBCF, $0 \leq x \leq 0.4$) 阴极在 900 °C 下使用 RA446 连接体时的 Cr 沉积过程。结果表明,Cr 沉积量的差异与 Sr 和 Ba 的含量密切相关,而与 LSBCF 阴极的电化学活性无关。随着 LSBCF 中 Sr 含量的降低,阴极上的 Cr 沉积量显著减少。Xie 等^[77]设计的 Ba 掺杂的 $\text{La}_{0.4}\text{Ba}_{0.2}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ 阴极,在铬暴露测试中表面铬沉积物含量显著低于 LSCF 阴极。此外,表面沉积物中主要是优先形成的 BaCrO_4 及少量的 SrCrO_4 。Zhen 等^[78]的研究表明,在使用 Fe-Cr 合金连接体时, $\text{La}_{0.6}\text{Ba}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ 阴极上的铬沉积量显著少于 LSCF 阴极,并且沉积物对 ORR 的毒化作用相对较小。Chen 等^[79]通过直接混合 LSCF 和 BCFN 制备了一种新的阴极材料($\text{La}_{0.24}\text{Sr}_{0.16}\text{Ba}_{0.6}$)($\text{Co}_{0.5}\text{Fe}_{0.44}\text{Nb}_{0.06}$) $\text{O}_{3-\delta}$ (LSBCFN)。LSBCFN 兼具 BCFN 的结构稳定性和 LSCF 的高电导率,且具有比单独 BCFN 和 LSCF 更好的电催化活性和铬中毒的耐受性。相似地,Zhao 等^[80]基于 $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ (SSC) 和 BCFN 设计了 $\text{Sm}_{0.5(1-x)}\text{Sr}_{0.5(1-x)}\text{Ba}_x\text{Co}_{1-0.3x}\text{Fe}_{0.2x}\text{Nb}_{0.1x}\text{O}_{3-\delta}$ (SSBCFN) 阴极。当 $x=0.5$ 时,SSBCFN5 表现出 SSC 的高电导率和 BCFN 的高氧扩散率和结

构稳定性。电化学测试结果的表明,SSBCFN5 在 SOFCs 的运行条件下具有优异的稳定性和抗毒化能力。最近,Zhou 等^[81]通过第一性原理计算提出阴离子 F 的掺杂可以提高 LSCF 阴极材料的铬容忍性,Sr 位和 La 位对 Cr 原子的吸附是一种弱的物理吸附,而在空位和 O 位上是化学吸附。因此,F 掺杂可以削弱 LSCF 表面对铬物种的吸附强度,从而提高 LSCF 阴极的铬耐受性。

近年来,高熵氧化物在耐腐蚀涂层和电化学催化等领域引起了广泛的关注^[82-83]。这类具有高构型熵的钙钛矿材料已经被用作为 SOFCs 的阴极材料,并且表现出优异的电化学性能和结构稳定性^[84-86]。Yang 等^[87]基于 LSM 阴极开发了一种高熵材料 $\text{La}_{0.2}\text{Pr}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$,A 位阳离子的高分散性引发了晶格畸变,导致了 Sr 周围形成了无序的应力场,进而限制了 Sr 向表面迁移。为了强化 LSCF 阴极的耐铬毒化的能力,Li 等^[88]在 A 位使用稀土和碱土元素掺杂,设计了一系列新型高熵钙钛矿作为 SOFCs 的阴极材料。在高熵材料的设计时,研究者将 La、Sr 和 Pr 作为选定元素,通过比较 8 个候选材料的性能将 A 位元素的活性排序为 $\text{Y} > \text{Ba} > \text{Sm} > \text{Nd}$ 。由此设计的高熵阴极($\text{La}_{0.2}\text{Sr}_{0.2}\text{Pr}_{0.2}\text{Y}_{0.2}\text{Ba}_{0.2}$) $\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSPYB) 表现出优异的 ORR 活性和铬耐受性。在含铬气氛下,高熵 LSPYB 在 41 d 的测试期间的衰减速率仅为 $0.25\% \text{ kh}^{-1}$,而 LSCF 在第 1 d 的测试中的极化阻抗值就增加了一倍。

当前,大多数的研究集中在传统阴极材料(如 LSM, LSCF 等)的抗铬毒化性能强化^[28, 67]。实际上,其他具有优异电催化活性的阴极材料也同样面临着严重的铬中毒问题,如 BSCF, BCFN, $\text{LnBaCo}_2\text{O}_{5+\delta}$, $\text{PrNiO}_{4+\delta}$ 等^[89-92]。Gao 等^[93]在 $\text{SrCo}_{0.9}\text{Ta}_{0.1}\text{O}_{3-\delta}$ (SCT) 阴极的基础上报道了一种 B 位中熵阴极 $\text{SrCo}_{0.5}\text{Fe}_{0.2}\text{Ti}_{0.1}\text{Ta}_{0.1}\text{Nb}_{0.1}\text{O}_{3-\delta}$ (SCFTTN),通过电化学测试、物理化学表征及理论计算,SCFTTN 表现出比 SCT 更好的铬耐受能力可以归因于熵稳定的相结构显著抑制了表面 Sr 的偏析。结合双钙钛矿的高氧扩散能力和高熵材料的优异特性,Zhu 等^[94]报道了具有高 ORR 催化活性和优异耐久性的高熵 $\text{Pr}_{0.2}\text{Sm}_{0.2}\text{Nd}_{0.2}\text{Gd}_{0.2}\text{La}_{0.2}\text{BaCo}_2\text{O}_{5+\delta}$ (PSNGLBC) 阴极,相较于 $\text{PrBaCo}_2\text{O}_{5+\delta}$ (PBC) 阴极,PSNGLBC 阴极能够抑制表面 Ba 元素的偏析。Zhu 等详细地比较了 LSCF、PBC 和 PSNGLBC 在干/湿空气和铬污染存在时对称电池的电化学性能和稳定性,如图 6a 和图 6b 所示。无论是在干燥还是潮湿的

含 Cr 气氛下, PSNGLBC 表现出最小的极化阻抗值和最优异的稳定性。通过对不同测试时间获得的阻抗谱进行弛豫时间分布(DRT)的分析(图 6c), Zhu 等认为中频阻抗的增加主要是由于表面偏析的物质改变了阴极表面附近的化学计量比, 并且表面沉积的铬物种阻挡了表面活性位点; 低频阻抗的增加可能是大量沉积的铬物种堵塞了阴极的孔隙, 进而影响了阴极中的气体扩散。Han 等^[95]在无钴阴极 $\text{PrBaFe}_2\text{O}_{5+\delta}$ (PBF) 的基础上进行高熵掺杂制备了

$\text{La}_{0.2}\text{Pr}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Gd}_{0.2}\text{BaFe}_2\text{O}_{5+\delta}$ (LPNSGBF)。在铬中毒测试中, 使用 LPNSGBF 阴极的单电池衰减速率为 $0.17\% \text{ h}^{-1}$, 远低于 PBF 阴极的 $0.79\% \text{ h}^{-1}$ 。Li 等^[96]在 BSCF 的基础上利用高通量计算设计了一种结合 BSCF 与 Nd、Ni、Zr 三元掺杂的阴极材料 $\text{Ba}_{0.4}\text{Nd}_{0.1}\text{Sr}_{0.5}\text{Co}_{0.6}\text{Ni}_{0.1}\text{Zr}_{0.1}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BNSCNZF)。与 BSCF 相比, BNSCNZF 在电子电导率、氧吸附等方面表现出更优异的性能。图 6d 描述了 SOFCs 的阴极上铬中毒和 CO_2 中毒的相关机制和反应过程。

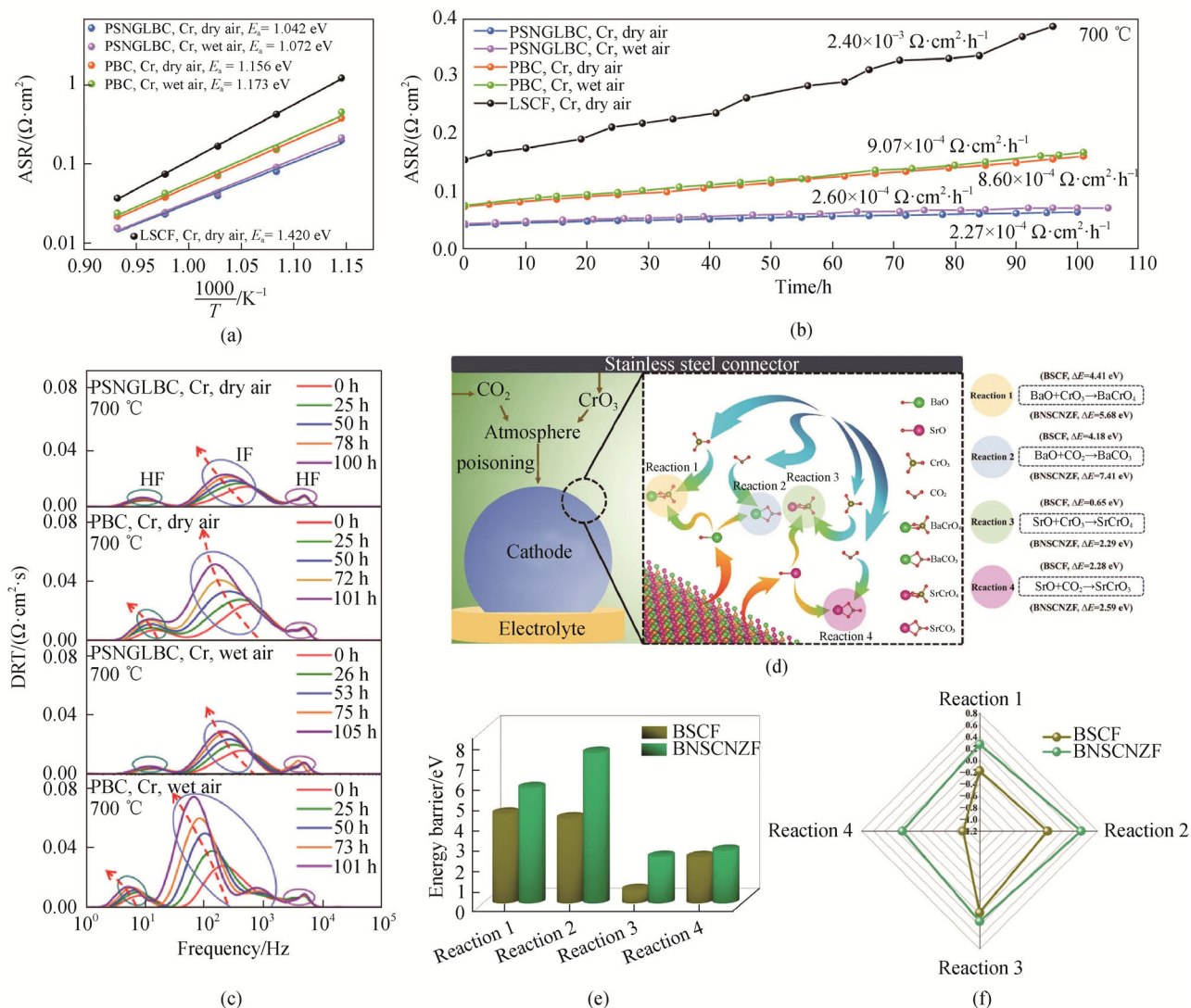


图 6 (a)在 600~800 °C, 对称电池在干/湿空气中暴露于 Cr 污染时的面积比阻抗值及活化能^[94]; (b)应用 PSNGLBC、PBC 和 LSCF 电极的对称电池在 700 °C 的面积比阻抗稳定性^[94]; (c)不同测试时间的 PSNGLBC 和 PBC 电极的阻抗谱对应的 DRT 分析^[94]; (d)阴极 Cr 中毒和 CO_2 中毒机理及途径的示意图^[96]; (e)BSCF 和 BNSCNZF 中杂相的形成能垒^[96]; (f)从晶格中产生杂相的吸附能^[96]

Fig. 6 (a) Polarization impedance and activation energy of symmetrical cells exposed to Cr contamination in dry/wet air at 600 to 800 °C^[94]; (b) Impedance stabilities of symmetrical cells with PSNGLBC, PBC, and LSCF electrodes in dry/wet air with Cr contamination at 700 °C^[94]; (c) Corresponding DRT analysis of the electrochemical impedance spectroscopy curves of PSNGLBC and PBC electrodes measured at different times^[94]; (d) Schematic of mechanisms and pathways of Cr poisoning and CO_2 poisoning on the cathode^[96]; (e) Energy barriers of the formation of produced phase impurities in BSCF and BNSCNZF^[96]; (f) Absorption energies of produced phase impurities from the lattice^[96]

Li 等将 BNSCNZF 强化的耐 Cr 和耐 CO₂ 毒化的能力归因于以下 2 个方面: 1) 在 BNSCNZF 中, 杂相的形成具有更高的反应能垒(图 6e); 2) 从 BNSCNZF 中形成惰性杂相需要更高的吸附能(图 6f)。

3 总结与展望

深入研究并采取措施来缓解阴极材料上的铬中毒问题, 对于进一步推动 SOFCs 技术的商业化进程至关重要。本文梳理了近年来在提升 SOFCs 阴极材料的耐铬毒化性能方面的重要进展。文中介绍了针对阴极材料上铬沉积现象所提出的相关理论机制, 并总结了当前已报道的多种能够有效缓解阴极材料铬中毒的策略。

尽管当前的研究取得了显著的进展, 但仍然面临着诸多挑战: 1) 用单一的理论似乎无法完美地解释不同的阴极材料上或者阴极材料与电解质界面处的铬沉积现象。对于不同的材料在不同的测试条件下, 这些机制可能同时发生或者是相互竞争。此外, 在 H-SOFCs 体系当中, 由于水蒸气的存在和质子的引入, 这一过程可能更为复杂。虽然有部分研究者开始关注 H-SOFCs 的铬中毒问题, 但目前尚无详细讨论 H-SOFCs 体系中铬中毒相关机制的文献。2) 重新设计或者改进已经商业化的连接体材料面临着较高的成本。在连接体上添加保护性涂层是一种可行的方式, 但也需要考虑额外工序所增加的成本。3) 对阴极材料进行表面修饰能够有效地强化其耐铬能力。但是孤立的纳米颗粒可能无法实现对内在脆弱的阴极的完全覆盖, 未覆盖的阴极表面可能仍然会受到二氧化碳、铬蒸汽和水蒸气等污染物的毒化。如果浸渍的表面修饰物被用作气态铬物种的优先反应物, 在长时间的运行时可能会被不断地消耗。尽管所形成沉积物的毒化效果较轻, 但是过多的积累量仍将会占据阴极上的活性位点并且阻碍阴极中气体的扩散。4) 耐毒化高熵材料的设计需要兼顾催化活性和稳定性, 因此掺杂元素的选择至关重要。此外, 不同的金属阳离子在高熵阴极中的相互作用机制目前尚不清楚, 仍需要进一步的深入研究。5) 近年来, SOFCs 在电解模式下的应用取得了显著的进展。在燃料电池模式下, 空气侧的电极材料发生的是阴极极化; 而在电解池模式下, 空气侧的电极上发生的是阳极极化。因此, 铬中毒的相关机制和毒化程度均会有所不同。然而, 当前对电解模式下的铬中毒研究还相对较少。

综上所述, 材料的铬中毒问题是 SOFCs 及其他

高温电化学设备中长期存在的挑战。未来还需要进一步探究不同运行条件下的铬中毒机制, 优化阴极材料的组成和结构, 以提高其在实际工业应用上的稳定性和可靠性, 进而推动 SOFCs 技术的商业化进程。

参考文献:

- [1] 国务院新闻办公室. 中国的能源转型[EB/OL]. (2024-08-29) [2024-11-05]. https://www.gov.cn/zhengce/202408/content_6971115.htm.
- [2] 人民日报. 新型储能技术助力高质量发展[EB/OL]. (2023-08-08)[2024-11-05]. http://paper.people.com.cn/rmrbwap/html/2023-08/08/nw.D110000renmrb_20230808_1-20.htm.
- [3] BRETT D J L, ATKINSON A, BRANDON N P, et al. Intermediate temperature solid oxide fuel cells[J]. Chem Soc Rev, 2008, 37(8): 1568–1578.
- [4] BRANDON N P, SKINNER S, STEELE B C H. Recent advances in materials for fuel cells[J]. Annu Rev Mater Res, 2003, 33: 183–213.
- [5] SINGHAL S C. Solid oxide fuel cells for stationary, mobile, and military applications[J]. Solid State Ion, 2002, 152: 405–410.
- [6] WACHSMAN E D, LEE K T. Lowering the temperature of solid oxide fuel cells[J]. Science, 2011, 334(6058): 935–939.
- [7] CHEN Y B, ZHOU W, DING D, et al. Advances in cathode materials for solid oxide fuel cells: Complex oxides without alkaline earth metal elements[J]. Adv Energy Mater, 2015, 5(18): 1500537.
- [8] ZHU F, HE F, XU K, et al. Enhancing the oxygen reduction reaction activity and durability of a double-perovskite via an A-site tuning[J]. Sci China Mater, 2022, 65(11): 3043–3052.
- [9] SUN C W, HUI R, ROLLER J. Cathode materials for solid oxide fuel cells: A review[J]. J Solid State Electrochem, 2010, 14(7): 1125–1144.
- [10] DING D, LI X X, LAI S Y, et al. Enhancing SOFC cathode performance by surface modification through infiltration[J]. Energy Environ Sci, 2014, 7(2): 552–575.
- [11] ZHU F, DU Z W, XU K, et al. Entropy and composition regulations of air electrodes enable efficient oxygen reduction and evolution reactions for reversible solid oxide cells[J]. Adv Energy Mater, 2024, 14(37): 2401048.
- [12] SHAO Z P, ZHOU W, ZHU Z H. Advanced synthesis of materials for intermediate-temperature solid oxide fuel cells[J]. Prog Mater Sci, 2012, 57(4): 804–874.
- [13] CHOI S, KUCHARCZYK C J, LIANG Y G, et al. Exceptional power density and stability at intermediate temperatures in protonic ceramic fuel cells[J]. Nat Energy, 2018, 3(3): 202–210.
- [14] DUAN C, TONG J, SHANG M, et al. Readily processed protonic ceramic fuel cells with high performance at low temperatures[J]. Science, 2015, 349(6254): 1321–1326.
- [15] RICHTER J, HOLTAPPELS P, GRAULE T, et al. Materials design for perovskite SOFC cathodes[J]. Monatsh Für Chem Chem Mon, 2009, 140(9): 985–999.
- [16] JIANG S P. A comparison of O₂ reduction reactions on porous (La, Sr)MnO₃ and (La, Sr)(Co, Fe)O₃ electrodes[J]. Solid State Ion, 2002, 146(1–2): 1–22.
- [17] SHAO Z P, HAILE S M. A high-performance cathode for the next generation of solid-oxide fuel cells[J]. Nature, 2004, 431: 170–173.
- [18] ZHOU W, RAN R, SHAO Z P. Progress in understanding and development of Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ}-based cathodes for intermediate-temperature solid-oxide fuel cells: A review[J]. J Power Sources, 2009,

- 192(2): 231–246.
- [19] ZHANG K, GE L, RAN R, et al. Synthesis, characterization and evaluation of cation-ordered $\text{LnBaCo}_2\text{O}_{5+\delta}$ as materials of oxygen permeation membranes and cathodes of SOFCs[J]. *Acta Mater*, 2008, 56(17): 4876–4889.
- [20] HERNÁNDEZ A M, MOGNI L, CANEIRO A. $\text{La}_2\text{NiO}_{4+\delta}$ as cathode for SOFC: Reactivity study with YSZ and CGO electrolytes[J]. *Int J Hydrog Energy*, 2010, 35(11): 6031–6036.
- [21] YANG Z B, GUO M Y, WANG N, et al. A short review of cathode poisoning and corrosion in solid oxide fuel cell[J]. *Int J Hydrog Energy*, 2017, 42(39): 24948–24959.
- [22] PEI K, ZHOU Y C, DING Y, et al. An improved oxygen reduction reaction activity and CO_2 -tolerance of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ achieved by a surface modification with barium cobaltite coatings[J]. *J Power Sources*, 2021, 514: 230573.
- [23] WANG F F, KISHIMOTO H, ISHIYAMA T, et al. A review of sulfur poisoning of solid oxide fuel cell cathode materials for solid oxide fuel cells[J]. *J Power Sources*, 2020, 478: 228763.
- [24] JIANG S P, ZHANG J P, ZHENG X G. A comparative investigation of chromium deposition at air electrodes of solid oxide fuel cells[J]. *J Eur Ceram Soc*, 2002, 22(3): 361–373.
- [25] ZHOU L F, MASON J H, LI W Y, et al. Comprehensive review of chromium deposition and poisoning of solid oxide fuel cells (SOFCs) cathode materials[J]. *Renew Sustain Energy Rev*, 2020, 134: 110320.
- [26] FERGUS J W. Metallic interconnects for solid oxide fuel cells[J]. *Mater Sci Eng A*, 2005, 397(1–2): 271–283.
- [27] HOLT A, KOFSTAD P. Electrical conductivity and defect structure of Cr_2O_3 . II. Reduced temperatures ($< \sim 1000^\circ\text{C}$) [J]. *Solid State Ion*, 1994, 69(2): 137–143.
- [28] JIANG S P, CHEN X B. Chromium deposition and poisoning of cathodes of solid oxide fuel cells—A review[J]. *Int J Hydrog Energy*, 2014, 39(1): 505–531.
- [29] HORITA T. Chromium poisoning for prolonged lifetime of electrodes in solid oxide fuel cells - Review[J]. *Ceram Int*, 2021, 47(6): 7293–7306.
- [30] 王天闻, 闫肃, 赵梦园, 等. 固体氧化物电池空气电极铬中毒机理及抗铬性能研究进展[J]. *化工学报*, 2024, 75(6): 2091–2108.
WANG Tianwen, YAN Su, ZHAO Mengyuan, et al. *CIESC J*, 2024, 75(6): 2091–2108.
- [31] HUANG J Y, CHEN Z Y, LUO Y J, et al. Advancements in chromium-tolerant air electrode for solid oxide cells: A mini-review[J]. *J Fuel Chem Technol*, 2025, 53(2): 249–259.
- [32] EBBINGHAUS B B. Thermodynamics of gas phase chromium species: The chromium oxides, the chromium oxyhydroxides, and volatility calculations in waste incineration processes[J]. *Combust Flame*, 1993, 93(1–2): 119–137.
- [33] BEEZ A, YIN X Y, MENZLER N H, et al. Insight into the reaction mechanism of $(\text{La}_{0.58}\text{Sr}_{0.40})(\text{Co}_{0.20}\text{Fe}_{0.80})\text{O}_{3-\delta}$ Cathode with volatile chromium species at high current density in a solid oxide fuel cell stack[J]. *J Electrochem Soc*, 2017, 164(10): F3028–F3034.
- [34] GINDORF C, SINGHEISER L, HILPERT K. Chromium vaporisation from Fe, Cr base alloys used as interconnect in fuel cells[J]. *Steel Res*, 2001, 72(11–12): 528–533.
- [35] GINDORF C, SINGHEISER L, HILPERT K. Vaporisation of chromia in humid air[J]. *J Phys Chem Solids*, 2005, 66(2–4): 384–387.
- [36] HILPERT K, DAS D, MILLER M, et al. Chromium vapor species over solid oxide fuel cell interconnect materials and their potential for degradation processes[J]. *J Electrochem Soc*, 1996, 143(11): 3642–3647.
- [37] BADWAL S P S, DELLER R, FOGER K, et al. Interaction between chromia forming alloy interconnects and air electrode of solid oxide fuel cells[J]. *Solid State Ion*, 1997, 99(3–4): 297–310.
- [38] MIZUSAKI J, TAGAWA H. Nonstoichiometry and thermochemical stability of the perovskite-type $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$ [J]. *Solid State Ion*, 1991, 49: 111–118.
- [39] KONYSHEVA E, PENKALLA H, WESSEL E, et al. Chromium poisoning of perovskite cathodes by the ODS alloy $\text{Cr}_5\text{Fe}_1\text{Y}_2\text{O}_3$ and the high chromium ferritic steel crofer 22APU [J]. *J Electrochem Soc*, 2006, 153(4): A765–A773.
- [40] MIYOSHI K, IWAI H, KISHIMOTO M, et al. Chromium poisoning in (La, Sr) MnO_3 cathode: Three-dimensional simulation of a solid oxide fuel cell[J]. *J Power Sources*, 2016, 326: 331–340.
- [41] JIANG S, ZHANG J, APATEANU L, et al. Deposition of chromium species at Sr-doped LaMnO_3 electrodes in solid oxide fuel cells I. Mechanism and kinetics[J]. *J Electrochem Soc*, 2000, 147(11): 4013–4022.
- [42] TANIGUCHI S, KADOWAKI M, KAWAMURA H, et al. Degradation phenomena in the cathode of a solid oxide fuel cell with an alloy separator[J]. *J Power Sources*, 1995, 55(1): 73–79.
- [43] WEI B, CHEN K F, ZHAO L, et al. Chromium deposition and poisoning at $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ oxygen electrodes of solid oxide electrolysis cells[J]. *Phys Chem Chem Phys*, 2015, 17(3): 1601–1609.
- [44] JIANG S, ZHANG S, ZHEN Y. Early interaction between Fe–Cr alloy metallic interconnect and Sr-doped LaMnO_3 cathodes of solid oxide fuel cells[J]. *J Mater Res*, 2005, 20(3): 747–758.
- [45] JIANG S, ZHANG J, FOGER K. Deposition of chromium species at Sr-doped LaMnO_3 electrodes in solid oxide fuel cells II. Effect on O_2 reduction reaction[J]. *J Electrochem Soc*, 2000, 147(9): 3195–3205.
- [46] JIANG S, ZHANG J, FOGER K. Deposition of chromium species at Sr-doped LaMnO_3 electrodes in solid oxide fuel cells III. Effect of air flow[J]. *J Electrochem Soc*, 2001, 148(7): C447–C455.
- [47] JIANG S P, ZHEN Y D. Mechanism of Cr deposition and its application in the development of Cr-tolerant cathodes of solid oxide fuel cells[J]. *Solid State Ion*, 2008, 179(27–32): 1459–1464.
- [48] FERGUS J W. Effect of cathode and electrolyte transport properties on chromium poisoning in solid oxide fuel cells[J]. *Int J Hydrog Energy*, 2007, 32(16): 3664–3671.
- [49] YOKOKAWA H, HORITA T, SAKAI N, et al. Thermodynamic considerations on Cr poisoning in SOFC cathodes[J]. *Solid State Ion*, 2006, 177(35–36): 3193–3198.
- [50] CHEN X B, HUA B, PU J, et al. Interaction between (La, Sr) MnO_3 cathode and Ni–Mo–Cr metallic interconnect with suppressed chromium vaporization for solid oxide fuel cells[J]. *Int J Hydrog Energy*, 2009, 34(14): 5737–5748.
- [51] ZHANG W Y, YAN D, YANG J, et al. A novel low Cr-containing Fe–Cr–Co alloy for metallic interconnects in planar intermediate temperature solid oxide fuel cells[J]. *J Power Sources*, 2014, 271: 25–31.
- [52] GROLIG J G, FROITZHEIM J, SVENSSON J E. Coated stainless steel 441 as interconnect material for solid oxide fuel cells: Oxidation performance and chromium evaporation[J]. *J Power Sources*, 2014, 248: 1007–1013.
- [53] HASSAN M A, BIN MAMAT O, MEHDI M. Review: Influence of alloy addition and spinel coatings on Cr-based metallic interconnects of solid oxide fuel cells[J]. *Int J Hydrog Energy*, 2020, 45(46): 25191–25209.
- [54] PALCUT M, MIKKELSEN L, NEUFELD K, et al. Improved oxidation resistance of ferritic steels with LSM coating for high temperature

- electrochemical applications[J]. *Int J Hydrog Energy*, 2012, 37(9): 8087–8094.
- [55] MOLIN S, CHEN M, HENDRIKSEN P V. Oxidation study of coated crofer 22 APU steel in dry oxygen[J]. *J Power Sources*, 2014, 251: 488–495.
- [56] LENKA R K, PATRO P K, SHARMA J, et al. Evaluation of $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_3$ protective coating on ferritic stainless steel interconnect for SOFC application[J]. *Int J Hydrog Energy*, 2016, 41(44): 20365–20372.
- [57] ZHAO Y T, JIANG Y N, ZHANG L J, et al. CuFe_2O_4 nano-spherical powder directly served as interconnect coating for solid oxide fuel cells applications[J]. *J Power Sources*, 2024, 599: 234221.
- [58] ZHAO Q Q, GENG S J, CHEN G, et al. Application of sputtered NiFe_2 alloy coating for SOFC interconnect steel[J]. *J Alloys Compd*, 2018, 769: 120–129.
- [59] KALU A W, LI X M, ZHOU L F, et al. Strategies to Counter Cr poisoning on air electrodes of solid oxide cells[J]. *Int J Hydrog Energy*, 2025, 101: 85–104.
- [60] HEO S J, HONG J, APHALE A, et al. Chromium poisoning of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3\pm\delta}$ cathodes and electrochemical validation of chromium getters in intermediate temperature-solid oxide fuel cells[J]. *J Electrochem Soc*, 2019, 166(13): F990–F995.
- [61] UDDIN M A, APHALE A, HU B X, et al. Electrochemical validation of in-cell chromium getters to mitigate chromium poisoning in SOFC stack[J]. *J Electrochem Soc*, 2017, 164(13): F1342–F1347.
- [62] AHMAD ISHFAQ H, KHAN M Z, SHIRKE Y M, et al. A heuristic approach to boost the performance and Cr poisoning tolerance of solid oxide fuel cell cathode by robust multi-doped ceria coating[J]. *Appl Catal B Environ*, 2023, 323: 122178.
- [63] ZHAO L, AMARASINGHE S, JIANG S P. Enhanced chromium tolerance of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ electrode of solid oxide fuel cells by $\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95}$ impregnation[J]. *Electrochem Commun*, 2013, 37: 84–87.
- [64] HAN X, SHAO Q, LI K X, et al. Constructing chromium-tolerance $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ cathode for solid oxide fuel cells using entropy-assisted surface engineering[J]. *Chem Eng J*, 2025, 503: 158480.
- [65] CHEN K F, AI N, O'DONNELL K M, et al. Highly chromium contaminant tolerant BaO infiltrated $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ cathodes for solid oxide fuel cells[J]. *Phys Chem Chem Phys*, 2015, 17(7): 4870–4874.
- [66] LIU W, KONYSHEVA E Y. Conductivity of SrCrO_4 and its influence on deterioration of electrochemical performance of cathodes in solid oxide fuel cells[J]. *ECS Trans*, 2014, 59(1): 327–332.
- [67] HUANG J Y, LIU Q, JIANG S P, et al. Promotional role of BaCO_3 on the chromium-tolerance of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ cathodes of solid oxide fuel cells[J]. *Appl Catal B Environ*, 2023, 321: 122080.
- [68] PEI K, ZHOU Y C, XU K, et al. Enhanced Cr-tolerance of an SOFC cathode by an efficient electro-catalyst coating[J]. *Nano Energy*, 2020, 72: 104704.
- [69] CHEN Y, YOO S, LI X X, et al. An effective strategy to enhancing tolerance to contaminants poisoning of solid oxide fuel cell cathodes[J]. *Nano Energy*, 2018, 47: 474–480.
- [70] HUANG J Y, LIANG F J, ZHAO S C, et al. Heterogeneous catalyst coating for boosting the activity and chromium tolerance of cathodes for solid oxide fuel cells[J]. *Adv Funct Mater*, 2024, 34(26): 2310402.
- [71] NIU Y H, ZHOU Y C, LV W Q, et al. Enhancing oxygen reduction activity and Cr tolerance of solid oxide fuel cell cathodes by a multiphase catalyst coating[J]. *Adv Funct Mater*, 2021, 31(19): 2100034.
- [72] ZHOU Y C, ZHANG W L, KANE N, et al. An efficient bifunctional air electrode for reversible protonic ceramic electrochemical cells[J]. *Adv Funct Mater*, 2021, 31(40): 2105386.
- [73] ZHU F, HE F, LIU D L, et al. A surface reconfiguration of a perovskite air electrode enables an active and durable reversible protonic ceramic electrochemical cell[J]. *Energy Storage Mater*, 2022, 53: 754–762.
- [74] ZHANG H, XU K, HE F, et al. Surface regulating of a double-perovskite electrode for protonic ceramic fuel cells to enhance oxygen reduction activity and contaminants poisoning tolerance[J]. *Adv Energy Mater*, 2022, 12(26): 2200761.
- [75] ZHEN Y D, TOK A I Y, BOEY F Y C, et al. Development of Cr-tolerant cathodes of solid oxide fuel cells[J]. *Electrochem Solid State Lett*, 2008, 11(3): B42–B46.
- [76] CHEN X, ZHANG L, JIANG S P. Chromium deposition and poisoning on $(\text{La}_{0.6}\text{Sr}_{0.4-x}\text{Ba}_x)(\text{Co}_{0.2}\text{Fe}_{0.8})\text{O}_3$ ($0 \leq x \leq 0.4$) Cathodes of Solid Oxide Fuel Cells [J]. *J Electrochem Soc*, 2008, 155(11): B1093.
- [77] XIE M Y, CAI C K, LIU X J, et al. Improved durability of high-performance intermediate-temperature solid oxide fuel cells with a Ba-doped $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ cathode[J]. *ACS Appl Mater Interfaces*, 2022.
- [78] ZHEN Y D, JIANG S P. Characterization and performance of $(\text{La}, \text{Ba})(\text{Co}, \text{Fe})\text{O}_3$ cathode for solid oxide fuel cells with iron–chromium metallic interconnect[J]. *J Power Sources*, 2008, 180(2): 695–703.
- [79] CHEN X B, JIANG S P. Highly active and stable $(\text{La}_{0.24}\text{Sr}_{0.16}\text{Ba}_{0.6})(\text{Co}_{0.5}\text{Fe}_{0.44}\text{Nb}_{0.06})\text{O}_{3-\delta}$ (LSBCFN) cathodes for solid oxide fuel cells prepared by a novel mixing synthesis method[J]. *J Mater Chem A*, 2013, 1(15): 4871–4878.
- [80] ZHAO L, CHENG Y, JIANG S P. A new, high electrochemical activity and chromium tolerant cathode for solid oxide fuel cells[J]. *Int J Hydrog Energy*, 2015, 40(45): 15622–15631.
- [81] ZHOU Y J, LÜ Z, ZHANG R Y, et al. Mechanism of chromium poisoning on $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.25}\text{Fe}_{0.75}\text{O}_3$ cathode and enhancing chromium tolerance using a novel anion doping strategy[J]. *Int J Hydrog Energy*, 2024, 85: 114–119.
- [82] ROST C M, SACHET E, BORMAN T, et al. Entropy-stabilized oxides[J]. *Nat Commun*, 2015, 6: 8485.
- [83] OSES C, TOHER C, CURTAROLO S. High-entropy ceramics[J]. *Nat Rev Mater*, 2020, 5(4): 295–309.
- [84] LIU Z Q, TANG Z J, SONG Y F, et al. High-entropy perovskite oxide: A new opportunity for developing highly active and durable air electrode for reversible protonic ceramic electrochemical cells[J]. *Nanomicro Lett*, 2022, 14(1): 217.
- [85] XU Y S, XU X, BI L. A high-entropy spinel ceramic oxide as the cathode for proton-conducting solid oxide fuel cells[J]. *J Adv Ceram*, 2022, 11(5): 794–804.
- [86] HE F, ZHU F, LIU D L, et al. A reversible perovskite air electrode for active and durable oxygen reduction and evolution reactions via the A-site entropy engineering[J]. *Mater Today*, 2023, 63: 89–98.
- [87] YANG Y, BAO H, NI H, et al. A novel facile strategy to suppress Sr segregation for high-entropy stabilized $\text{La}_{0.6}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$ cathode[J]. *J Power Sources*, 2021, 482: 228959.
- [88] LI Z, GUAN B, XIA F, et al. High-entropy perovskite as a high-performing chromium-tolerant cathode for solid oxide fuel cells[J]. *ACS Appl Mater Interfaces*, 2022, 14(21): 24363–24373.
- [89] KIM Y, CHEN X B, JIANG S P, et al. Chromium deposition and

- poisoning at $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ cathode of solid oxide fuel cells[J]. *Electrochem Solid State Lett*, 2011, 14(4): B41–B45.
- [90] GU H T, CHEN H, ZHENG Y F, et al. Effect of chromium poisoning on the electrochemical properties of $\text{NdBaCo}_2\text{O}_{5+\delta}$ cathode for IT-SOFCs[J]. *Int J Hydrog Energy*, 2010, 35(6): 2457–2462.
- [91] WEI B, SCHROEDER M, MARTIN M. Surface cation segregation and chromium deposition on the double-perovskite oxide $\text{PrBaCo}_2\text{O}_{5+\delta}$ [J]. *ACS Appl Mater Interfaces*, 2018, 10(10): 8621–8629.
- [92] SCHRÖDL N, EGGER A, LAMMER J, et al. Long-term stability of $\text{Pr}_2\text{NiO}_{4+\delta}$ air electrodes for solid oxide cells against chromium poisoning [J]. *J Electrochem Soc*, 2021, 168(1): 014509.
- [93] GAO Y, HUANG X Q, YUAN M K, et al. A medium entropy cathode with enhanced chromium resistance for solid oxide fuel cells[J]. *J Eur Ceram Soc*, 2023, 43(5): 2002–2012.
- [94] ZHU F, XU K, HE F, et al. An active and contaminants-tolerant high-entropy electrode for ceramic fuel cells[J]. *Acs Energy Lett*, 2024, 9(2): 556–567.
- [95] HAN X, LING Y H, YANG Y, et al. Utilizing high entropy effects for developing chromium-tolerance cobalt-free cathode for solid oxide fuel cells[J]. *Adv Funct Mater*, 2023, 33(43): 2304728.
- [96] LI Z Y, SUN H B, ZHAO F L, et al. High-entropy cathodes with Cr and CO_2 tolerance via the combination of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ and Nd, Ni, Zr ternary doping for both oxygen ion and proton conducting solid oxide fuel cells[J]. *Adv Compos Hybrid Mater*, 2024, 8(1): 87.

Development on Enhancing the Tolerance of Solid Oxide Fuel Cell Cathodes Against Cr Poisoning

ZHU Feng, CHEN Yu

(School of Environment and Energy, South China University of Technology, Guangzhou 510006, China)

Extended Abstract

Solid oxide fuel cells (SOFCs) are an extremely attractive energy conversion technology due to their high efficiency, low emissions, and flexible fuels, which have wide application prospects in distributed power generation and hydrogen production. The operating temperatures of conventional SOFCs are typically above 1000 °C. The high operating temperatures impose stricter requirements on the materials of various components in the SOFCs system, especially in terms of mechanical strength, reactivity, thermal expansion behavior, and cell sealing. Also, the high operating temperatures lead to long start-up times and weak economic competitiveness of the SOFCs, seriously hindering the commercialization of SOFC technology. Reducing the operating temperatures to intermediate temperatures (*i.e.*, 600–800 °C) can significantly mitigate the chemical reactions between cell components, extend the service life, and expand the range of cheaper material options, thus enhancing its economic competitiveness. However, the kinetics of oxygen reduction reaction (ORR) related to the cathodes of SOFCs become notably sluggish with the fall in temperature, resulting in a rapid increase in polarization impedance and a significant decrease in cell performance. It is thus crucial to develop cathode materials with superior electrocatalytic activity and durability for ORR at intermediate temperatures.

Although significant progress has been made in developing cathode materials with high performance and excellent durability at intermediate temperatures, the electrochemical evaluation of developed cathode materials has been performed under relatively mild conditions in most studies. However, cathodes of SOFC stacks are inevitably exposed to harsh working conditions under realistic operating conditions. For instance, the gas supplied to the cathodes may contain steam, CO_2 , sulfide, *etc.*. In addition, the system components of the stacks will volatilize gaseous contaminants (*e.g.*, CrO_3 and $\text{CrO}_2(\text{OH})_2$, *etc.*) at operating temperatures. These gaseous contaminants can deposit on the surface of cathodes or react directly with cathodes, resulting in poisoning and/or corrosion of the cathode materials. In particular, Cr poisoning on the cathode is one of the problems widely concerned.

Compared with conventional ceramic interconnects, metallic interconnects widely used at intermediate temperatures can reduce the cost, and exhibit higher electrical and thermal conductivity, as well as better machinability. However, a certain amount of Cr is usually added to metallic interconnects to improve their oxidation and corrosion resistance. At high temperatures and oxidizing atmosphere, the Cr_2O_3 layer formed on the surface of metallic interconnects will evaporate gaseous chromium vapor. These gaseous Cr species are prone to react with alkaline earth metal oxides (such as BaO and SrO) that are segregated on the cathode surface, forming solid deposits on the cathode surface and/or at the interface between the cathode and electrolyte. These inert deposits occupy the active sites for oxygen reactions on the cathode, leading to a significant decrease in electrocatalytic activity, and affect the gas diffusion in the porous cathode, resulting in rapid degradation of the cell. It is thus essential for maintaining the robustness of the SOFCs system and extending its service life to alleviate the Cr poisoning of the cathodes.

Summary and prospects Conducting in-depth research and taking measures to mitigate Cr poisoning on the cathode materials is crucial for further advancing the commercialization of SOFCs technology. In this review, recent development in enhancing the Cr tolerance of cathodes is represented. The theoretical mechanisms of Cr deposition on cathodes are introduced, and the reported strategies to alleviate Cr poisoning on cathodes are summarized. Despite the significant progress made in the existing research, there are still some challenges to be addressed, *i.e.*, a) it seems that a single theory cannot perfectly explain the Cr deposition on different cathode materials. For different materials under different test conditions, these mechanisms may occur simultaneously or compete with each other. In addition, in proton-conducting SOFCs (H-SOFCs), these processes may be more complicated due to the

introduction of protons. Although some researchers deal with the problem of Cr poisoning in H-SOFCs, there are no detailed literature reports on the mechanism of Cr poisoning in H-SOFCs system; b) Redesigning or improving the currently commercialized interconnect materials faces high costs. Applying a protective coating on the interconnects is a feasible approach. However, the added cost of additional manufacturing processes also needs to be considered; c) The surface modification of cathodes can effectively strengthen its Cr resistance. However, isolated nanoparticles are unable to achieve complete coverage of the inherently fragile electrodes. The areas of the cathode surface that are not covered may be still poisoned by contaminants such as CO₂, Cr vapor, and steam. Moreover, if the impregnated surface catalysts are used as a preferred reactant of the gaseous Cr species, they may be continuously consumed for long periods of operation. Although the poisoning effect of the deposits is mild, excessive accumulation of the deposits will occupy the active sites for the oxygen reduction reaction and hinder the diffusion of gases in the cathode; d) The design of contaminants-tolerant high-entropy materials needs to balance electrocatalytic activity and stability. In addition, the interaction mechanisms of different metal cations in the high-entropy cathodes are still unclear and require further in-depth research; and e) Recent progress has been made in the application of SOFCs in electrolysis mode. As is known, the electrode material on the air side undergoes cathodic polarization in fuel cell mode, while in electrolysis mode, anodic polarization occurs on the electrode on the air side. Therefore, the mechanisms and degree of Cr poisoning will be different. Unfortunately, there is still a lack of relevant research on Cr deposition in electrolysis mode. In summary, the phenomenon of Cr poisoning in materials is a long-standing challenge for SOFCs and other high-temperature electrochemical devices. A future research should focus on the investigation on Cr poisoning mechanisms under various operating modes and optimization of the composition and structure of cathode materials. These efforts aim to enhance the stability and reliability of SOFCs in practical industrial applications, ultimately advancing the commercialization process of SOFCs technology.

Keywords solid oxide fuel cells; cathode; chromium poisoning; chromium tolerance