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Published in:
Gongneng Cailiao/Journal of Functional Materials

DOI:
10.3969/j.issn.1001-9731.2021.06.010

Published: 30/06/2021

Document Version
Peer reviewed version

固体氧化物燃料电池阴极材料的研究进展

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摘 要：阴极材料是固体氧化物燃料电池的重要组成。提高阴极材料的电子/离子电导率、降低极化电阻是使 SOFC 低温化运行、延长电池使用寿命的重要方法。阴极材料的高电子电导性促使钙钛矿结构氧化物在阴极材料的研究领域占据主导地位。本文综述了钙钛矿结构阴极、尖晶石结构阴极和 Ruddlesden-popper 型结构阴极材料的研究进展，并展望了未来阴极材料的发展方向。

关键词：固体氧化物燃料电池；阴极材料；钙钛矿氧化物；研究进展

中图分类号：TM911.4　　**文献标识码**：A

0 引 言

随着社会文明的发展和世界人口的迅速增长，人类生活对能源的需求也在持续增长。化石燃料作为主要的能源来源，为我们的社会生活提供了大量的资源。然而，化石燃料的过度消耗产生了大量的二氧化碳（CO_2）和杂质（SO_2、NO_x），引起了人们对环境污染和气候变化的担忧，对我们社会文明的健康发张造成威胁[1-5]。因此，为了实现可持续发展的未来，迫切需要可再生能源和绿色能源转换技术[6]。固体氧化物燃料电池（SOFC）的转换效率高达 85%，而且具有燃料灵活性大、低成本、安全稳定和大幅度降低 CO_2 排放量等优点，在能量转换、存储等领域具有巨大的发展前景[7, 8]。SOFC 的主要由阴极、阳极和固体电解质三部分构成[9-30]。其中，阴极是氧气发生还原反应的场所[31]。在阴极上，氧分子吸附解离后得到电子被还原成氧离子：$O_2 + 4e^- \rightarrow 2O^{2-}$。商业化的 SOFC 中，最常见的组合是 LSM/YSZ/Ni-YSZ，但氧化钇稳定氧化锆（YSZ）的使用温度居高不下。高温工作虽然有利于电极反应，然而长时间的高温状态会加速电池性能的衰减，极大地降低电池的使用寿命。因此降低其运行温度是 SOFC 发展的必然

收到初稿日期：2021-01-21　　**收到修改稿日期**：2021-03-02
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趋势。本文作者回顾了 SOFC 阴极材料的研究进展，并展望了其未来的发展方向。

1　SOFC 阴极材料的基本要求

阴极是 SOFC 体系中最重要的组成部件之一，其材料需要满足的条件有：首先是较高的电子电导率（＞100S·cm^{-1}）、一定的离子电导率。一定的离子电导率不但会提高催化反应，而且会增大氧离子的扩散能力，而较高的电子电导率可以显著降低欧姆损耗，提高转化效率。然后是对氧的电化学反应具有较高的催化活性、足够的孔隙率（20%~40%）以及良好的化学及物理稳定性。此外，还有一个重要的考虑因素是热膨胀系数（TEC）应能与相连的电解质相匹配。当电极材料与电解质材料的 TEC 不相容时，容易造成电池断裂、脱落，严重影响电池的稳定和正常运行[32]。

2　SOFC 阴极材料结构

SOFC 阴极材料种类众多，根据晶体结构不同可将其分为钙钛矿结构、尖晶石结构和 Ruddlesden-popper 型结构材料，如图 1 所示。

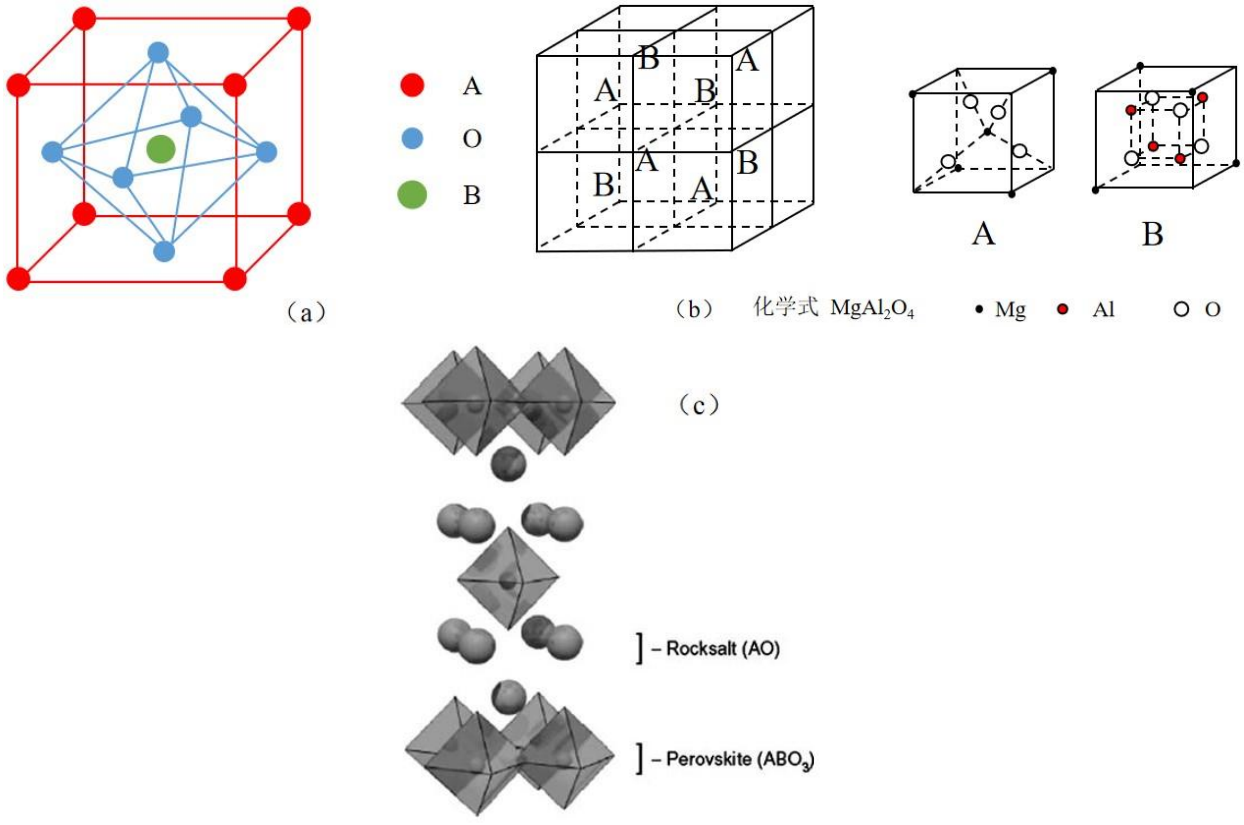

图 1. 常见阴极的结构种类：（a）钙钛矿结构；（b）尖晶石结构；（c）Ruddlesden-popper 型材料[33-45]

Fig 1. The structure types of common cathodes are as follows: (a) perovskite structure; (b) spinel structure; (c) Ruddlesden-popper type materials[33-45]

2.1 钙钛矿结构

钙钛矿结构氧化物在 SOFC 阴极材料中的应用非常广泛。标准的钙钛矿结构为立方晶系，可用 ABO_3 分子式表示，如图 1（a）所示，其中 A 位为稀土元素（如 La、Pr、Sm、Gd 和 Nd 等）和碱土金属元素（如 Sr、Ca 和 Ba 等），位于立方体的八个顶点，配位数为 12；B 位多是离子半径较小的过渡金属元素（如 Mn、Fe 和 Co 等），位于立方体的中心，配位数为 6；O 表示负 2 价的氧离子。影响钙钛矿催化活性的因素主要有两点：表面吸附氧和晶格氧。温度较低时，表面吸附氧起主要作用，由 B 位的过渡金属元素决定。温度较高时，晶格氧起作用，改变 A、B 位置的金属元素可以调节晶格氧的数量和活性，或者用二价阳离子部分替代晶格中 A、B 位离子产生晶格缺陷或晶格氧，提高催化活性。

2.1.1 $LaMnO_3$ 基阴极材料

锰酸镧（$LaMnO_3$）是 SOFC 中应用比较成熟的一种钙钛矿型材料，对还原反应具有良好的电子导电性和高催化活性，并且结构稳定。在钙钛矿氧化物阴极材料研究中，通过在 A、B 位置上掺杂或置换金属阳离子（如 Ba、Ca、Co、Mg、Ni、Sr、Y 等），可以形成更多氧离子空位，增大离子电导率[46]。如当 Sr 掺杂 $LaMnO_3$ 形成 $La_{1-x}Sr_xMnO_{3-\delta}$（LSM）时，$Sr^{2+}$阳离子部分取代 La^{3+}，同时发生锰离子氧化，有效地增加空位浓度，提高离子电导率[46]。因此，LSM 一直是 SOFC 阴极材料中研究最多地一种。研究发现，采用浸渍法对阴极进行表面改进，可以增大反应活性区，提高阴极性能，浸渍过程如图 2 所示[47-52]。氧气在传统阴极上的反应活性区较小，导致其催化活性和离子电导率都比较低。在阴极中加入高离子导电相（如 YSZ），可以构建出电子-离子复合纳米阴极，还原反应延伸到整个复合阴极，增大了反应活性区。Ju 等人采用浸渍技术将 LSM 纳米颗粒沉积到多孔 YSZ 骨架上，制备了 LSM-YSZ 复合阴极。阴极电导率随 LSM 浸渍量的增加而提高。阴极极化电阻（R_p）先随 LSM 浸渍的增加而减小，当负载约 4.5vol.%时，R_p 有最小值 0.569Ω·cm^2，然后随浸渍的增加而增大，如图 3 所示[53]。这是因为当 LSM 纳米颗粒沉积在 YSZ 晶粒表面时，会产生 LSM-YSZ 反应活性区。随着 LSM 纳米颗粒数的增加，反应活性区增大，R_p 降低，当 YSZ 表面被 LSM 颗粒充分覆盖时，反应活性区达到峰值，R_p 有最小值。浸渍量进一步增加时，多余的 LSM 纳米颗粒会阻碍气体的传输孔道，从而降低电化学的反应活性区，增大 R_p。此外，将 SDC 浸渍到 LSM 上可以制备 LSM-SDC 复合阴极。LSM-SDC 阴极的面积比电阻（ASR）随 SDC 浸渍量的增多而逐渐增大，浸渍量为 50wt.%时，有最小的 ASR 值 0.23Ω·cm^2。当 SDC 浸渍量进一步增多时，阴极 ASR 反而增大。这可能是由于 SDC 含量增多，孔隙率下降，从而增加浓度极化。

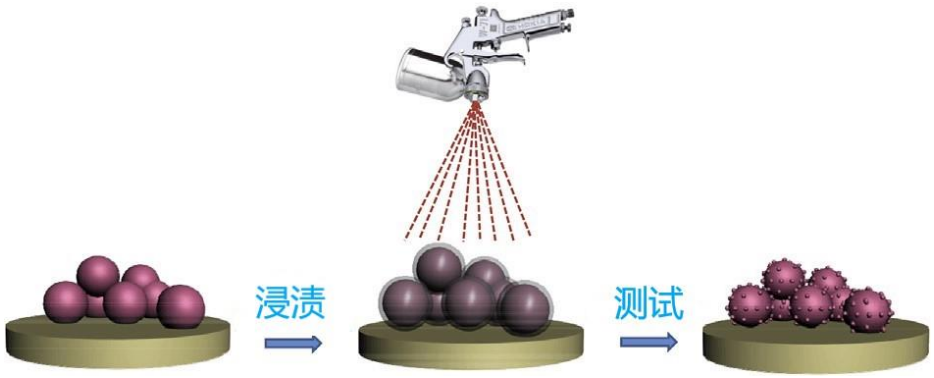

图 2. 喷雾浸渍工艺和阴极的形态变化[48]

Fig 2. Spray impregnation process and morphology change of cathode[48]

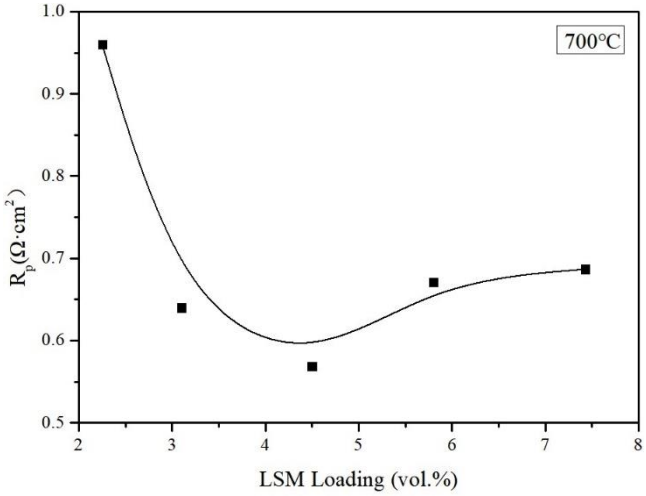

图 3. 700°C时，LSM 负载对极化电阻（R_p）的影响[53]

Fig 3. Effect of LSM loading on polarization resistance (R_p) at 700°C[53]

2.1.2 $LaCoO_3$ 基阴极材料

钴酸镧（$LaCoO_3$）也是 SOFC 中一种常用的钙钛矿结构材料，在相同的条件下，$LaCoO_3$ 比 $LaMnO_3$ 的电导率大很多。掺杂 Sr 的 $LaCoO_3$（$La_{1-x}Sr_xCoO_{3-\delta}$，LSC）在氧化环境中会形成大量的氧空气，增大氧扩散能力，提高离子电导率[54]。但是 LSC 材料并没有得到广泛的应用，原因是 Co 元素的出现使得 La 元素更易于从阴极层扩散至电解质层，并发生固相反应生成高电阻相的 $La_2Zr_2O_7$，而且所有掺 Sr 的钴阴极材料在 800°C时会和 YSZ 电解质反应生成 $SrZrO_3$ 绝缘相，导致极化电阻显著增大[55]。即 LSC 阴极与 YSZ 平台的电解质具有极强的反应性，LSC-YSZ 体系受到限制。为了对此进行控制，可以在阴极和电解质之间添加一个阻挡层（如 GDC、SDC），从而避免其他相的生成，但这种方法并不是很成功，因为 LSC 与 YSZ 存在较大的 TEC 失配问题。还有一种方法是用其他阳离子（如 Ni^{2+}、Fe^{3+}等）部分或全部取代 LSC 中的 Co^{3+}。其中，$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$（LSCF）具有较高的电子和离子电导率及适用的热膨胀特性，是 SOFC 中研究广泛的阴极材料，其功率密度与 LSM 类似，但工作温度比 LSM 低。近

几年对 LSCF 基阴极 SOFC 性能的研究如表 1 所示。

表 1. LSCF 基阴极的电池性能

Table 1 Battery performance of LSCF based cathode

阴极材料	制备方法	温度（℃）	功率密度（$mW·cm^{-2}$）	极化电阻（$Ω·cm^2$）	参考文献
LSCF-SDC $La_{0.6}Ca_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ}$-SDC	浸渍	600		0.15 0.16	[56]
$LSCF_{6482}$	喷雾浸渍	700	940	0.04	[48]
LSCF $La_{0.57}Ce_{0.03}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ $La_{0.54}Ce_{0.06}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$	溶胶凝胶	750		0.21 0.14 0.09	[57]
LSCF-$Ce_{0.8}Gd_{0.2}O_{1.9}$	喷雾热解沉积	600	500	0.27	[58]
LSCF-$Gd_{0.1}Ce_{0.9}O_{1.95}$	机械处理	800 750 700 650		0.08 0.17 0.38 0.69	[59]
LSCF 33.7wt.% YSB-LSCF 40.6wt.% YSB-LSCF	浸渍	550	46 103 167	4.93 2.04 1.06	[60]

LSCF：$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}$；SDC：$Ce_{0.8}Sm_{0.2}O_{1.9}$；YSB：$Y_{0.25}Bi_{0.75}O_{1.5}$

2.1.3 $LaFeO_3$ 基阴极材料

铁酸镧（$LaFeO_3$）钙钛矿也可以用作 SOFC 阴极，但是 $LaFeO_3$ 的电导率并不高，需要掺杂金属离子（如 Sr）以提高孔隙率，增大电导率[61]。Kammer Hansen 研究了以 $Ce_{1.9}Gd_{0.1}O_{1.95}$ 为电解质的（$La_{1-x}Sr_x$）$_{0.99}FeO_{3-δ}$（x=0、0.05、0.15、0.25、0.35、0.50、0.70）（LSF）阴极的电化学性能[62]。（$La_{1-x}Sr_x$）$_{0.99}FeO_{3-δ}$ 阴极的 TEC 随 Sr 含量的增加而增大。（$La_{1-x}Sr_x$）$_{0.99}FeO_{3-δ}$ 阴极的 ASR 先随 Sr 含量的增加而减小，当 Sr 含量 x=0.15 时，ASR 有最小值，之后 ASR 随着 Sr 含量的继续增大而增大，如图 4 所示。此外，在 700℃时，Sr 和 Ni 双掺杂的 $La_{1-x}Sr_xFe_{0.7}Ni_{0.3}O_{3-δ}$ 阴极的电导率从 $90S·cm^{-1}$（LSFN0）增加到最大值 $200S·cm^{-1}$（LSFN0.2），然后下降[61]。这是因为电导率与掺杂剂含量有关，适当的掺杂量可以增大电导率，降低阻抗，而过大的掺杂量则会提高浓度，增大浓度极化电阻。

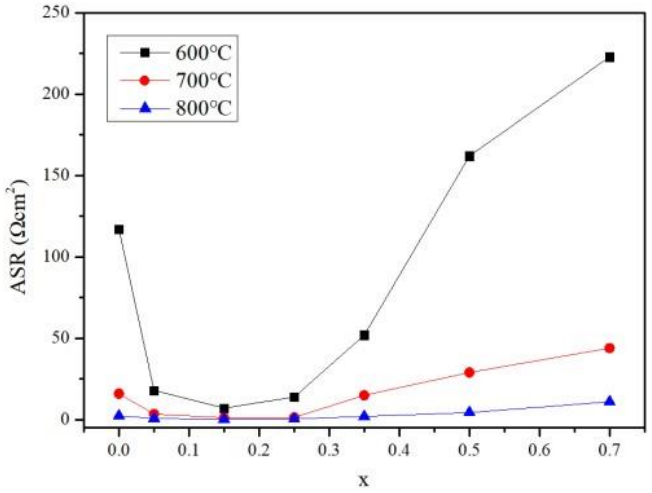

图 4. $(La_{1-x}Sr_x)_{0.99}FeO_{3-\delta}$(x=0、0.05、0.15、0.25、0.35、0.50、0.70)阴极的 ASR 与 Sr 含量的关系[62]

Fig 4. Relationship between ASR and Sr content of $(La_{1-x}Sr_x)_{0.99}FeO_{3-\delta}$(x=0、0.05、0.15、0.25、0.35、0.50、0.70) cathode[62]

2.2 尖晶石结构

尖晶石（AB_2O_4）型氧化物材料的性能主要是由二价（Mg^{2+}、Zn^{2+}等）、三价（Al^{3+}、Co^{3+}、Cr^{3+}等）离子的分布造成的。在 AB_2O_4 结构中，氧离子按立方紧密堆积排列，二价阳离子位于四面体空隙中，三价阳离子位于八面体空隙中，如图 1（b）所示。尖晶石材料具有化学稳定性强、高温下耐腐蚀性强以及热稳定性良好的优点，作为阴极材料已受到广泛的关注[39, 40, 63-67]。例如，$Mn_{1.5}Co_{1.5}O_4$（MCO）阴极材料，MCO 具有良好的热稳定性和结构稳定性，以及较高的电子电导率，是一种性能优异的 SOFC 阴极材料[68, 69]。与 MCO 阴极相比，SDC-MCO 复合阴极的电池性能明显下降。产生这个结果的主要原因是 MCO-SDC 复合阴极的电子电导率比 MCO 阴极低，以致 MCO-SDC 复合阴极的电流收集困难。研究发现，在 MCO-SDC 复合阴极上镀一层集流层可以显著改善电池性能。例如，将具有良好混合电子-离子导电性的钙钛矿氧化物 $Sm_{0.5}Sr_{0.5}CoO_3$ 涂覆到 MCO-SDC 复合阴极上，其峰值功率密度比 MCO、MCO-SDC 阴极都高，甚至显著高于同等条件下的 LSM-YSZ 阴极。孙克宁团队提出一种新的 $CuCo_2O_4$ 尖晶石型阴极材料，在 800、750 和 700℃时的极化电阻分别为 0.12、0.25 和 0.4Ω·cm²，峰值功率密度达 972、800 和 620mW·cm^{-2}[63]。$CuCo_2O_4$ 材料具有半导体特性，电导率随着温度的升高而增加，800℃时的电导率为 114S·cm^{-1}。同时，$CuCo_2O_4$ 阴极与氧化钪稳定氧化锆（SSZ）电解质的 TEC 相近，说明 $CuCo_2O_4$ 材料与 SOFC 组件相匹配，可以作为 SOFC 阴极材料长期运行。将 $CuCo_2O_4$ 作为前驱体浸渍到多孔 SSZ 电解质中，可以增大反应活性区，降低极化电阻，提高 SOFC 的电化学性能，如图 5 所示[70]。在 800℃时，浸渍阴极的极化电阻降低至 0.087Ω·cm²，

是目前尖晶石结构材料的最佳性能。最近，Li 研究报道了 $FeCo_2O_{4-x}Ce_{0.8}Sm_{0.2}O_{1.9}$（x=0、30、40、50、60、70wt.%）复合氧化物作为 SOFC 阴极材料的性能研究[39]。$Ce_{0.8}Sm_{0.2}O_{1.9}$ 的加入对 $FeCo_2O_4$-$xCe_{0.8}Sm_{0.2}O_{1.9}$ 复合材料的物理和电化学性能起着关键作用。其中，$FeCo_2O_4$-$60Ce_{0.8}Sm_{0.2}O_{1.9}$ 复合阴极在 800℃下具有最好的电催化活性，峰值功率密度为 397mW·cm^{-2}，在空气中的极化电阻为 0.094Ω·cm^2，远小于 $FeCo_2O_4$ 阴极的极化电阻 4.18Ω·cm^2，如图 6 所示。这种电化学性能的显著改善主要是由于反应活性区的延伸和氧化物离子电导率的增加。

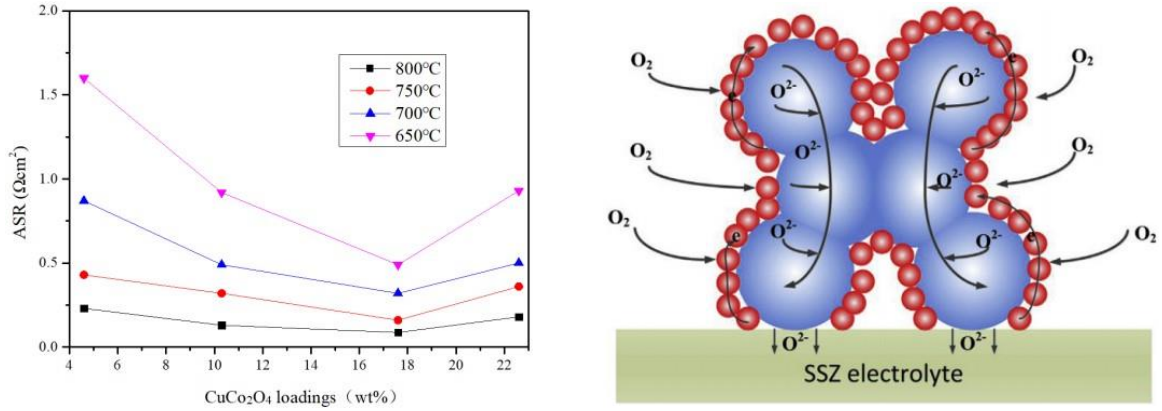

图 5. 浸渍 $CuCo_2O_4$ 阴极的 ASR 及其结构示意图[70]

Fig 5. ASR of impregnated $CuCo_2O_4$ cathode and its structure diagram[70]

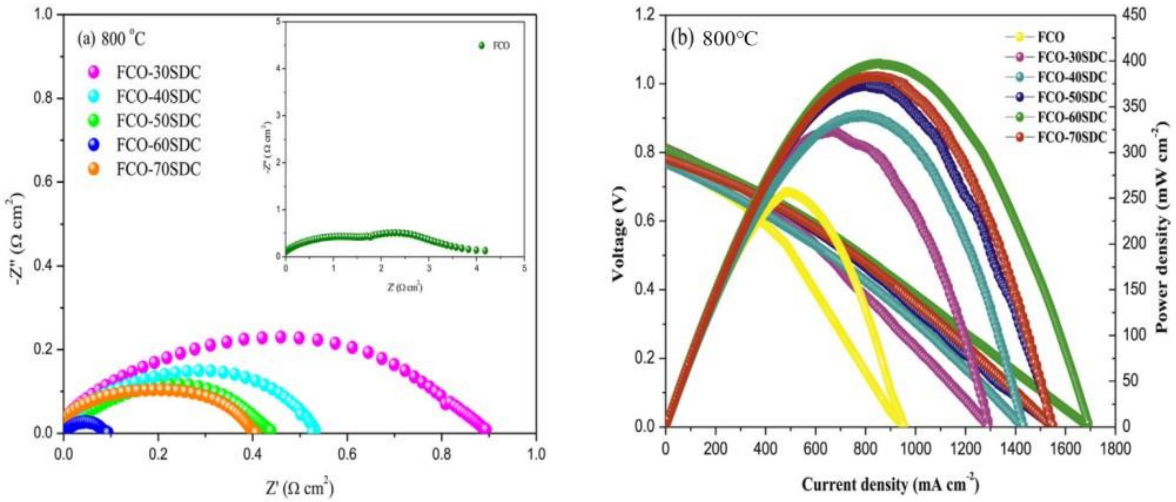

图 6.（a）FCO-xSDC|SDC|FCO-xSDC（x=0、30、40、50、60、70wt.%）对称电池的电化学阻抗谱；（b）~400μm SDC 电解质支撑的 FCO-xSDC（x=0、30、40、50、60、70wt.%）复合阴极的放电曲线（干 H_2 为燃料；空气为氧化剂）[39]

Fig 6. (a) The electrochemical impedance spectroscopy of FCO-xSDC|SDC|FCO-xSDC（x=0、30、40、50、60、70 wt.%）symmetry battery; (b) Discharge curve of FCO-xSDC（x=0、30、40、50、60、70wt.%）composite cathode supported by ~400μm SDC electrolyte (dry H_2 as fuel; Air as oxidant) [39]

2.3 Ruddlesden-popper 型结构

Ruddlesden-popper（R-P）型结构材料可以用（ABO_3）$_n$AO（A=稀土/碱金属元素；B=过渡金属元素）来表示，其结构可以看做是 n 层四方钙钛矿（ABO_3）$_n$ 与 AO 交互层叠排列，如图 1（c）所示。这种材料具有较高的氧扩散系数和表面交换系数，显著提高了阴极材料的活性。最常用的体系是 n=1 的相，它具有典型的 K_2NiF_4 结构。例如，$La_2NiO_{4+\delta}$ 就具有这种典型的结构特性，具有良好的电化学催化活性，但其与电解质的兼容性比较差，900℃时，$La_2NiO_{4+\delta}$ 与 GDC 电解质有明显的化学反应[71-78]。据报道通过 La 位或 Ni 位的取代可以优化这个体系[79-81]。例如，Sr 和 Co 双掺杂的 $La_{2-x}Sr_xNi_{1-x}Co_xO_{4+\delta}$ 阴极具有优异的电化学性能。Zheng 等人提出用软化学法合成 $La_2Ni_{0.5}Cu_{0.5}O_4$ 和 $Pr_2Ni_{0.5}Cu_{0.5}O_4$ 氧化物作为 SOFC 阴极材料，$La_2Ni_{0.5}Cu_{0.5}O_4$ 和 $Pr_2Ni_{0.5}Cu_{0.5}O_4$ 阴极的 TEC 分别为（10.0-13.5）×$10^{-6}K^{-1}$ 和（9.0-11.2）×$10^{-6}K^{-1}$，与常用的电解质 $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}$（12.2×$10^{-6}K^{-1}$）、$Ce_{0.8}Gd_{0.2}O_{1.9}$（12.5×$10^{-6}K^{-1}$）等拥有较好的相容性[82]。在 300~800℃范围内，$Pr_2Ni_{0.5}Cu_{0.5}O_4$ 阴极的电导率都超过 100S·cm^{-1}，特别是在 450℃时，电导率有最大值 130S·cm^{-1}，如图 7 所示。以 $Pr_2Ni_{0.5}Cu_{0.5}O_4$ 为阴极制备的 $Pr_2Ni_{0.5}Cu_{0.5}O_4$|$Ce_{0.8}Gd_{0.2}O_{1.9}$|Ni-8YSZ 电池在 800℃时的最大功率密度为 130mW·cm^{-2}。Garali 等人采用机械球磨法合成了 Eu 掺杂的 $La_{2-x}Eu_xNiO_{4+\delta}$（$x$=0、0.2、0.4、0.6、0.8）（$LENO_x$）材料[83]。研究发现，$LENO_x$|SDC|$LENO_x$ 对称电池在空气中的 R_p 与 Eu 的掺杂量有关。当 Eu=0.2 时，700℃下 $LENO_{0.2}$ 的 R_p 有最小值 1.3Ω·cm^2，如图 8 所示。

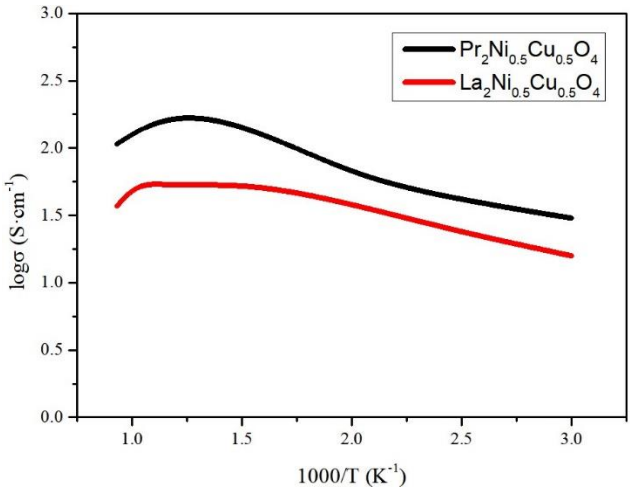

图 7. LNC 和 PNC 阴极电导率与温度的关系[82]

Fig 7. Relationship between cathode conductivity and temperature of LNC and PNC[82]

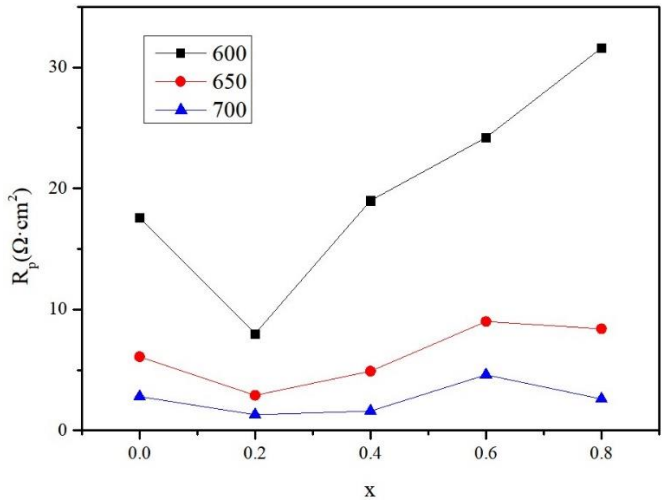

图 8. $LENO_x$|SDC|$LENO_x$ 对称电池的极化电阻和 Eu 掺杂量 x 的关系[83]

Fig 8. Relationship between polarization resistance and Eu doping amount x of $LENO_x$|SDC|$LENO_x$ symmetrical cell[83]

3 结论与展望

SOFC 是一种将化学能直接转化为电能的能源转换装置，是解决能源紧缺问题的重要技术。多孔阴极是 SOFC 的重要结构，因此研究 SOFC 低温运行时性能优良的阴极材料是延长电池寿命、降低电池成本的关键。研究较多的 $LaMnO_3$ 基阴极、$LaCoO_3$ 基阴极和 $LaFeO_3$ 基阴极材料都属于钙钛矿结构氧化物，它们的电化学催化活性大小为：$LaFeO_3$＜$LaMnO_3$＜$LaCoO_3$。钙钛矿结构阴极材料的电子、离子电导性受掺杂剂的影响较大，A 位掺杂（如 Sr^{2+}）可以提高材料的离子电导率，B 位掺杂（如 Co）可以提高材料的电子导电性。此外，还有尖晶石结构阴极和 Ruddlesden-popper 型结构阴极材料，都具备优良的氧扩散性能和电化学活性，也是研究较多的 SOFC 阴极材料，拥有良好的研发潜力。综上可知，具备良好的电子/离子电导率、催化活性和氧扩散性能等优点的阴极及其复合材料，必然是 SOFC 阴极材料的研究焦点。

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Research progress of cathode materials in solid oxide fuel cells

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Abstract：Cathode material is an important component of solid oxide fuel cell. Improving the electron / ion conductivity of cathode materials and reducing the polarization resistance are important methods to make SOFC operate at low temperature and increase the service life of battery. The high electronic conductivity of cathode materials makes perovskite oxides occupy a dominant position in the research field of cathode materials. In this paper, the research progress of perovskite structure cathode, spinel structure cathode and Ruddlesden-popper structure cathode materials was reviewed, and the development direction of cathode materials in the future was prospected.

Keywords：Solid Oxide Fuel Cell (SOFC)；Cathode materials；perovskite oxides；Research progress