

BaO 改性阳极平管型固体氧化物燃料电池的直接甲醇发电特性

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摘 要: 针对甲醇燃料固体氧化物燃料电池(SOFC)镍基阳极存在的积碳问题, 采用湿法浸渍对平管型 SOFC 的 Ni/氧化钇稳定氧化锆(YSZ)阳极表面进行 BaO 修饰改性, 提升电池的抗积碳性能。结果表明: 在 750 °C、水碳比(摩尔比)为 0.75 条件下, 基于甲醇燃料的平管型 SOFC 经过 BaO 阳极表面改性后, 在 0.8 V 时的功率密度由 326.72 mW/cm² 增加至 452.87 mW/cm²。以 200 mA/cm² 进行恒流放电长期耐久性测试, 平管型 SOFC 经过 BaO 阳极表面改性后, 稳定运行时间由 4 h 提升至 500 h, 改性后的阳极表面未发现碳沉积。BaO 阳极表面改性可提升电池中甲醇内重整效率, 有效提高甲醇燃料 SOFC 的耐久性。

关键词: 平管型固体氧化物燃料电池; 氧化锆; 甲醇; 耐久性; 积碳

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化石资源的大量使用对环境造成严重影响, 节能减排成为当前发展的焦点。固体氧化物燃料电池(SOFC)因其出众的能量转化效率、广泛的燃料适用范围、无污染和可有效利用的高质量余热等优点, 吸引了众多研究者的关注^[1-2]。氢气是 SOFC 的理想燃料, 但是氢气的体积能量密度低, 需要将其置于高压环境让其液化, 因此储存运输困难^[3]。此外氢气有较高的易燃性和易爆性, 并且会在金属材料内扩散, 引发氢脆效应^[4]。为避免氢气这些特性带来的风险, 氢气的推广使用需要建造大量针对性的基础设施。因此, 迫切需要寻找一种来源广泛且绿色环保的燃料来打破 SOFC 被氢气束缚的窘境。

在常温常压下, 甲醇呈液态, 体积能量密度远高于氢气(甲醇的体积能量密度为 15.80 MJ/L, 氢气仅有 8.50 MJ/L^[5-6]), 使甲醇在储运方面较氢气更为便捷, 是优秀的储氢介质。另外甲醇已经有相当成熟的生产工艺, 工业生产普遍采用一氧化碳、二氧化碳加压催化氢化法合成甲醇, 也能利用植物和生活垃圾提取合成^[7-8]。

SOFC 可直接使用甲醇进行内重整发电, 如 Xu 等^[9]采用以 Sr₂Fe_{1.5}Mo_{0.5}O₆ (SFMO)为阳极的电解质支撑电池在 800 °C 以甲醇和氢气为燃料时, 电池的峰值功率密度($P_{\max}$)分别为 391 mW/cm² 和 520 mW/cm²。Wang 等^[10]使用表面修饰 Ru/Ce_{0.95}Ru_{0.05-x}O_{2-δ} (Ru/CR_{5-x}O)的镍-氧化钇稳定的氧化锆(Ni/YSZ)阳极支撑电池在 750 °C 以甲醇为燃料的 $P_{\max}$ 为 1.01 W/cm², 略低于氢气条件下的 1.22 W/cm²。这些研究进一步表明甲醇燃料 SOFC 具有较为优异的电化学性能, 电池输出功率接近 H₂ 条件的输出功率。然而, 使用以甲醇为燃料的 SOFC 时存在阳极积碳问题, 而积碳的形成不仅降低电池性能, 还会影响到阳极结构强度^[11]。Chiu 等^[12]直接使用甲醇作为镍基阳极 SOFC 的燃料时, 电池运行 100 h 后因积碳导致迅速衰减, 原因是纤维状积碳破坏了阳极的多孔结构。根据研究发现, 当甲醇作为 Ni/YSZ 阳极 SOFC 的燃料时, 甲醇会在 SOFC 内重整成氢气、一氧化碳、二氧化碳和微量的甲烷^[13-15], 而生成的一氧化碳和甲烷在电池中会分别发生积碳

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反应(Boudouard 反应和甲烷裂解),从而降低电池的耐久性^[16]。

为了提高甲醇 SOFC 的耐久性,研究者通常选择在燃料中添加大量的水,即选用高水碳比 $[r(S/C)$, 摩尔比]甲醇燃料。Chen 等^[17]研究了直接使用甲醇水作为 Ni/YSZ 阳极 SOFC 燃料的可行性,800 °C 电池使用 $r(S/C) = 1.5$ 的甲醇水溶液以 500 mA/cm² 的电流密度恒流稳定运行,结果表明阳极没有出现积碳现象。但是,加入大量水会导致燃料稀释,从而降低燃料的体积能量密度,同时也增大了燃料汽化的能耗,降低系统效率^[18-19]。

因此为了兼顾抗积碳能力和电化学性能,大量研究采用其它阳极材料代替传统的 Ni/YSZ 阳极,例如 Hu 等^[20]使用 Ni/Ce_{0.7}Sn_{0.1}Sm_{0.2}O_{2-δ}(Ni/SSn₁₀DC) 阳极的电池在 700 °C 以氢气和甲醇为燃料时 $P_{\max}$ 分别为 1.99 W/cm² 和 2.11 W/cm²,700 °C 以甲醇为燃料时进行恒流(200 mA/cm²)放电测试, Ni/SSn₁₀DC 电压稳定输出超过 12 h,而对照组 Ni/Ce_{0.8}Sm_{0.2}O_{2-δ} (SDC)仅能稳定运行 4 h。Wang 等^[21]报道了使用 Cu-Sn 掺杂 SDC-YSZ 阳极在 800 °C 以甲醇为燃料时的 $P_{\max}$ 为 259.20 mW/cm²,运行 40 h 后 Raman 光谱测试未检测到积碳。韩敏芳等^[22]使用 Sr₂Ti_{0.8}Co_{0.2}FeO_{6-δ} 钙钛矿陶瓷作为阳极的电池,分别以甲烷、甲醇和乙醇为燃料的工况下,均能稳定运行 100 h。

另外,部分研究者通过采用表面改性的手段来提升镍基阳极的抗积碳能力。例如在阳极表面掺杂碱土金属氧化物来提升电池的抗积碳性能,从而提高电池的电化学性能和耐久性^[23-24]。如 Takeguchi 等^[25]使用 2.5%(质量分数)MgO 改性的镍基材料作为 SOFC 阳极,实现电池在 800 °C 的加湿甲烷(含水量 3%,体积分数)条件下 300 h 的稳定运行。Li 等^[26]采用 CaO 掺入 Ni/YSZ 阳极,将单位质量阳极(1 g)上的积碳产生速率从 0.05 g 积碳/min 降低至 0.02 g 积碳/min。另外,Liu 等^[27]通过原位 Raman 光谱发现, BaO 修饰镍基阳极可以缓解积碳,因为 BaO 会为改性后的阳极表面提供 OH⁻基团,与碳原子形成 CO₃²⁻基团,最后转化成二氧化碳。以上的研究结果证明碱土元素能提升 Ni/YSZ 阳极抗积碳能力,但是,目前缺少关于 BaO 改性对电池的甲醇转化率、抗积碳能力和电化学性能变化影响的研究。

本工作采取湿法浸渍对平管型阳极支撑电池的阳极表面进行改性。对比了在低水碳比 $[r(S/C) =$

0.75]的甲醇气氛下, BaO 改性前后的电池的放电特性与甲醇转化率。

1 实验

1.1 电池制备

使用的电池支撑阳极为氧化镍和摩尔分数为 3%Y₂O₃ 稳定 ZrO₂ (NiO-3YSZ), 阳极功能层为氧化镍和摩尔分数为 8%Y₂O₃ 稳定 ZrO₂ (NiO-8YSZ), 电解质、阻隔层和阴极分别为 8YSZ、Gd_{0.1}Ce_{0.9}O_{2-δ} (GDC) 和 La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ}-GDC (LSCF-GDC), 其中活性阴极面积为 60 cm², 电池标记为 NiO-3YSZ|NiO-8YSZ|8YSZ|GDC|LSCF-GDC。电池的材料与尺寸如表 1 所示, 电池的制造工艺可参考团队之前的工作^[28-30]。将此种未改性的电池记为 Ni/YSZ 电池。

表 1 平管型固体氧化物燃料电池的结构
Table 1 Configuration of flat-tube solid oxide fuel cell (SOFC)

Component	Material	Thickness
Anode support layer	NiO-3%(in mole) yttria-stabilized zirconia (NiO-3YSZ)	~1.5 mm
Active functional layer	NiO-8%(in mole) yttria-stabilized zirconia (NiO-8YSZ)	~15 μm
Electrolyte	8YSZ	15-20 μm
Barrier layer	Gd _{0.1} Ce _{0.9} O _{2-δ} (GDC)	3 μm
Cathode	La _{0.6} Sr _{0.4} Co _{0.2} Fe _{0.8} O _{3-δ} -GDC (LSCF-GDC)	15-20 μm

称取 15.68 g 的 Ba(NO₃)₂ 粉末,溶于 200 mL 去离子水中,在 70 °C 搅拌 2 h,得到用于浸渍的 0.3 mol/L 硝酸钡前驱体溶液。将 Ni/YSZ 电池的一端用蜡封住阳极孔道,将制备好的硝酸钡前驱体溶液(70 °C)通过进样器注射到电池的燃料通道中,随后在电池的另一端同样用蜡封住,将电池放入 50 °C 的烘箱保持 24 h 以保证钡溶液充分浸入阳极孔道,然后在 90 °C 干燥 1 h 用于去除蜡质,经过以上流程得到的电池记为 Ba-Ni/YSZ 电池。

1.2 样品表征

电池在升温还原后,以 0.60 L/min (SLM)氢气作为燃料气进行初始性能测试,使用甲醇作为燃料进行测试时,水蒸汽发生器将甲醇水溶液[水碳化 $r(S/C) = 0.75$]通入阳极,水蒸汽发生器温度设定为 130 °C,此时对应的甲醇流量为 0.30 g/min,阴极通入 5 L/min 空气。使用燃料电池测试设备(SOFC-100 W,无锡先导智能装备股份有限公司)和电化学工作站(VMP3B-20,法国 BioLogic 公司)测试电池不同工况下的电化学特性和耐久性,所有的阻抗测试频

率范围在 20 mHz~30 kHz, 交流幅值为 10 mV。对于测试中产生尾气采取干燥处理后使用在线气相色谱仪(GC7820, 山东鲁南分析仪器有限公司)进行成分分析。在电池完成耐久性测试后使用扫描电子显微镜(SEM, FEI Quanta FEG 250, 美国 FEI 公司)和能量色散 X 射线光谱仪(EDS)研究电池的微观形貌和元素分布。使用 Raman 光谱(inVia Reflex, 英国雷尼肖)分析进一步了解改性前后电池的积碳情况。

2 结果与讨论

2.1 微观结构分析

通过 SEM-EDS 分析 BaO 在平管型电池燃料孔道表面修饰效果。图 1a 为改性电池阳极燃料孔道表面的 SEM 照片。沿阳极燃料孔道进气的垂直方向在孔道表面取 3 点作为能谱点分析的测试位置, 图 1b 为选取位置的能谱点分析测试结果。由图 1b 可见, 在电池燃料极孔道处 Ba 的质量分数分别为 1.63%, 2.00% 和 1.39%, Ba 的平均质量分数为 1.67%, 这证明 Ba 元素有效修饰了 Ni/YSZ 电池阳极燃料孔道表面。

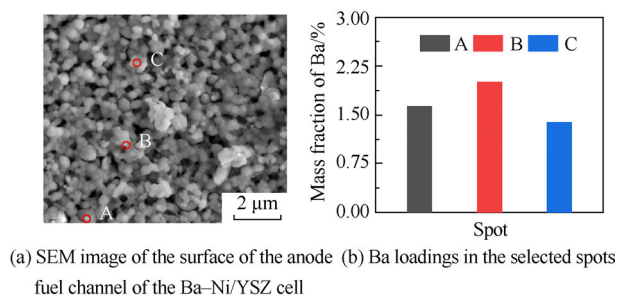


图 1 Ba-Ni/YSZ 电池的阳极侧燃料孔道微结构
Fig. 1 Micro-structure of the anode fuel channels of the Ba-Ni/YSZ cell

2.2 氢气条件下电化学性能分析

在氢气条件下, 测试了改性前后的电池在不同温度下发电性能, 结果如图 2 所示。图 2a 和图 2b 为 Ni/YSZ、Ba-Ni/YSZ 电池的电流-电压(I - V)特性, 在 750 °C, Ni/YSZ、Ba-Ni/YSZ 电池的开路电压(OCV)分别为 1.12、1.07 V, 说明电池气密性良好。在 750 °C, Ni/YSZ 和 Ba-Ni/YSZ 电池的 $P_{\max}$ 分别为 555.66、507.03 mW/cm², 说明钡改性对以氢气为燃料的平管型 SOFC 输出功率没有明显的影响。Ni/YSZ 和 Ba-Ni/YSZ 电池的放电性能都随着温度

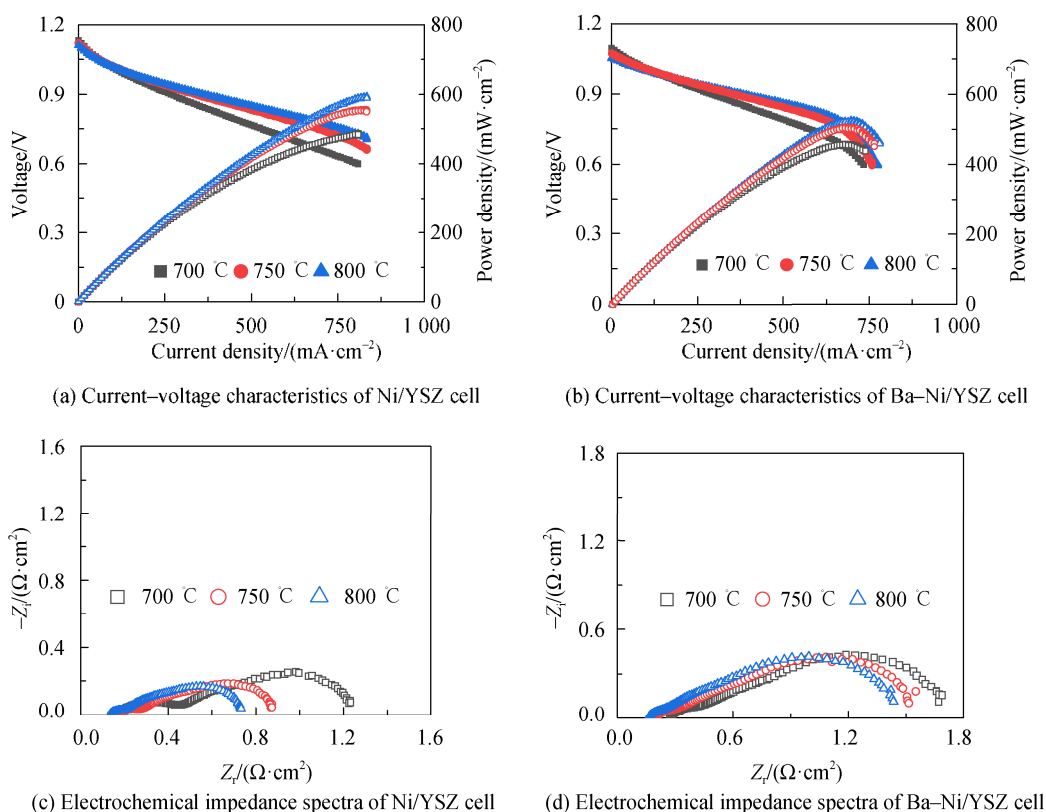


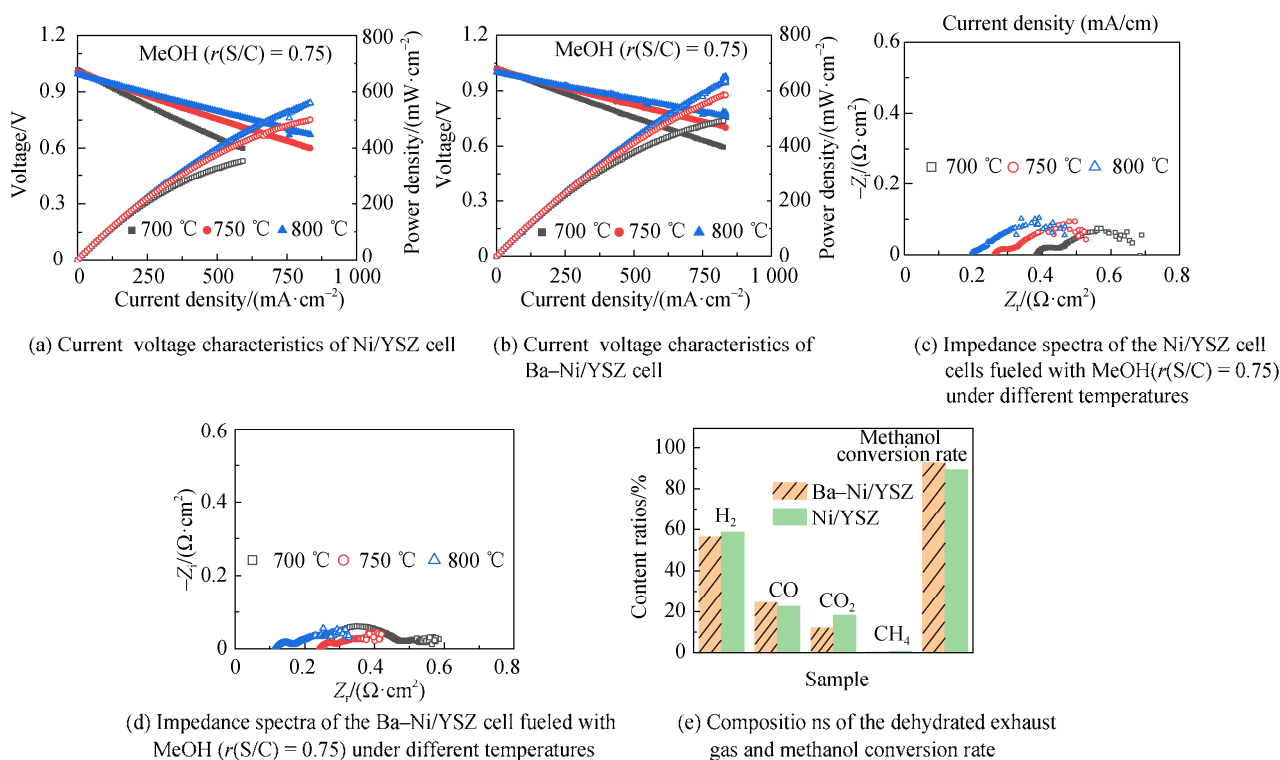
图 2 氢气下 Ni/YSZ 与 Ba-Ni/YSZ 电池的电化学性能
Fig. 2 Performances of the Ni/YSZ cell and Ba-Ni/YSZ cell under H₂

升高而提高, Ni/YSZ 电池在 700、750、800 °C 的 $P_{\max}$ 是 487.68、555.38 mW/cm² 和 592.25 mW/cm², Ba-Ni/YSZ 在对应温度下分别是 458.23、507.03 mW/cm² 和 525.68 mW/cm²。图 2c 和图 2d 为 Ni/YSZ 电池和 Ba-Ni/YSZ 电池的欧姆阻抗、极化阻抗, 它们均随着温度升高而变小, 两者的欧姆阻抗差别较小, 700 °C 两者欧姆阻抗分别是 0.20 $\Omega \cdot \text{cm}^2$ 和 0.27 $\Omega \cdot \text{cm}^2$; 两者微弱的性能差距主要受极化阻抗影响, 750 °C 时 Ni/YSZ 电池极化阻抗为 0.74 $\Omega \cdot \text{cm}^2$, Ba-Ni/YSZ 极化阻抗为 1.33 $\Omega \cdot \text{cm}^2$, 改性后电池因为钡的浸渍堵塞了阳极部分气体扩散通道, 导致气体在 Ni/YSZ 内的扩散过程受阻, 极化阻抗因此变大^[31-33]。

2.3 甲醇条件下电化学性能

图 3 为 Ni/YSZ 电池和 Ba-Ni/YSZ 电池在甲醇

气氛 [$r(\text{S/C}) = 0.75$] 下的电化学性能表现及 OCV 条件下甲醇转化率对比。图 3a 的 $I-V$ 特性曲线显示 Ni/YSZ 电池在 750 °C 时 0.8 V 下功率密度为 326.72 mW/cm², 而 Ba-Ni/YSZ 电池 0.8 V 下的功率密度为 452.87 mW/cm² (见图 3b)。由此可见, BaO 改性后的电池以甲醇为燃料时, 发电性能得到显著提高。由图 3c 和图 3d 可见, 该性能差异主要来自于极化阻抗, Ba-Ni/YSZ 电池极化阻抗明显小于 Ni/YSZ 电池。由图 3e 可见, 在 OCV 条件下 Ni/YSZ 电池与 Ba-Ni/YSZ 电池的甲醇转化率分别为 89.40% 和 92.70%, 这是由于在燃料孔道表面的 BaO 促进了甲醇在电池内转化, 阳极表面修饰 BaO 后增强 Ni 基阳极的亲水性, 进一步使水裂解为 OH⁻ 基团扩散在 Ni 表面位点, 与将吸附在 Ni 表面的 C 发生氧化反应^[34]。



$r(\text{S/C})$ is the ratio of steam to carbon.

图 3 甲醇条件下 Ni/YSZ 电池与 Ba-Ni/YSZ 电池性能
Fig. 3 Performance of the Ni/YSZ and Ba-Ni/YSZ cells under methanol

2.4 耐久性测试

耐久性评估是评估甲醇燃料 SOFC 的重要指标。为此以 750 °C、甲醇 [$r(\text{S/C}) = 0.75$]、200 mA/cm² 的条件测试了 Ni/YSZ 电池和 Ba-Ni/YSZ 电池耐久性性能, 如图 4 所示。Ni/YSZ 电池电化学性能在耐久性测试开始后不久就急剧恶化 (见图 4a), Ba-Ni/YSZ 电池

电压稳定, 稳定运行超过 500 h。Ba-Ni/YSZ 长期耐久性测试期间的尾气气相色谱结果分析 (见图 4b) 显示, 改性电池在耐久性测试中转化率稳定在 90% 以上。这表明钡元素修饰的燃料孔道能够使得甲醇在电池内稳定转化。图 4c 为 Ba-Ni/YSZ 电池在耐久性测试过程中 $I-V$ 极化曲线变化规律, OCV

基本保持稳定,说明电池气密性良好。电池的初始 $P_{\max}$ 为 584.87 mW/cm^2 , 100 h 时电池的 $P_{\max}$ 是 541.52 mW/cm^2 , 并逐步下降, 500 h 时电池的 $P_{\max}$

已降为 415.50 mW/cm^2 ; 随着运行时间的延长, 电池电压呈下降趋势, 电池初始放电电压为 0.94 V , 运行 500 h 后电压为 0.89 V , 衰减率为 $0.01\%/h$ 。

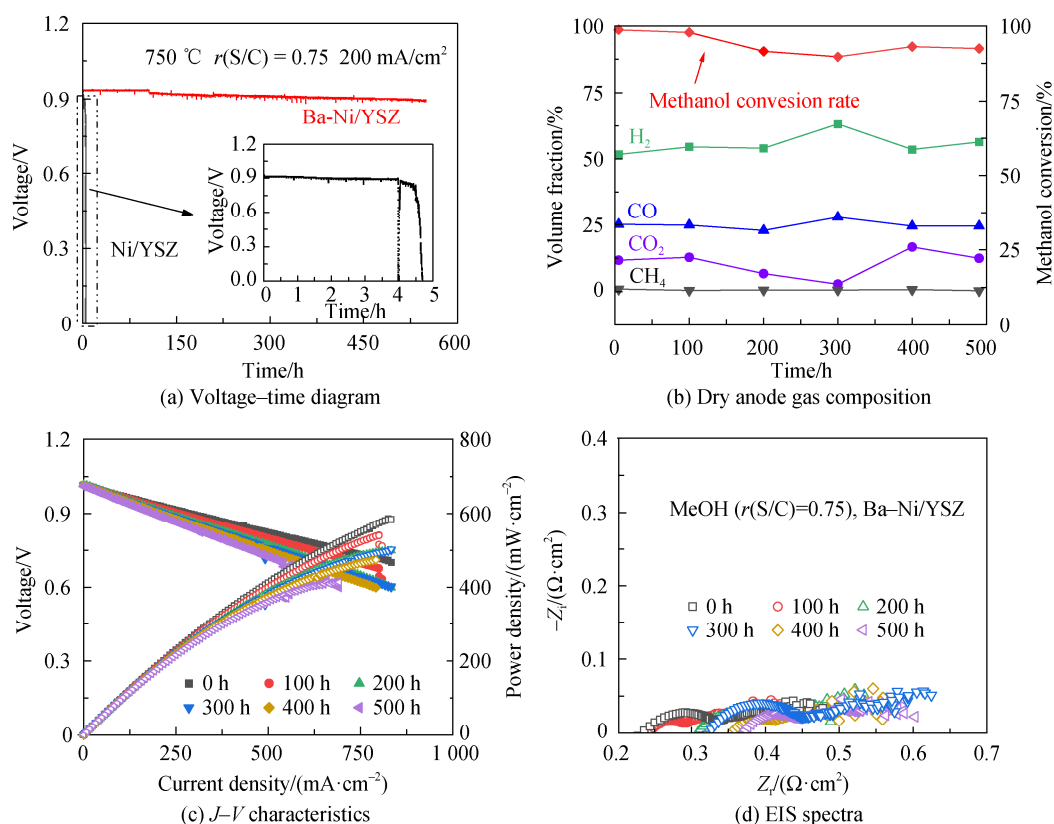


图4 750°C 、甲醇[$r(\text{S/C}) = 0.75$]、 200 mA/cm^2 下的 Ni/YSZ 及 Ba-Ni/YSZ 电池耐久性

Fig. 4 Durability of the Ni/YSZ and Ba-Ni/YSZ cells with methanol under $r(\text{S/C})=0.75$ at 750°C with current density of 200 mA/cm^2

为进一步研究衰减的原因,对电池的阻抗变化进行了分析,如图4d所示。电池在500 h的耐久性测试后,电池的欧姆阻抗从 $0.25 \Omega\cdot\text{cm}^2$ 增长到 $0.33 \Omega\cdot\text{cm}^2$, 极化阻抗从测试前的 $0.24 \Omega\cdot\text{cm}^2$ 增加到 $0.28 \Omega\cdot\text{cm}^2$ 。其中,欧姆阻抗增加的原因是由于甲醇燃料中含有一定量的水,且放电过程中会产生水,造成活性阳极镍损失,进而导致电池电化学性能有所衰减^[35]。

2.5 测试后电池微观形貌表征

通过 SEM 对耐久性测试前后的 Ba-Ni/YSZ 电池进气口处的阳极功能层形貌进行表征,结果如图5a和图5b所示。SEM 照片中白色区域代表 Ni 相、灰色区域代表 YSZ 相^[36-37]。与仅还原电池(见图5a)相比, Ba-Ni/YSZ 电池经过耐久性测试后在阳极功能层附近镍颗粒分布更加稀疏。为更精细地表征在阳极功能层附近镍颗粒变化情况(见图5c和图5d),采用图形处理软件 Image J 对 SEM 照片中的 Ni 颗

粒的粒径进行测量统计^[38-39],耐久性测试前后电池的 SEM 照片识别结果分别呈现在图5c和图5d中,电池阳极功能层的镍粒径平均尺寸由 $0.97 \mu\text{m}$ 降为 $0.92 \mu\text{m}$ 。这些结果说明耐久性测试后 Ba-Ni/YSZ 电池活性阳极出现明显的镍损失,从而导致了电池的电化学性能衰减^[40]。

为分析甲醇燃料 SOFC 的积碳分布情况,对经过长期耐久性测试后的电池入口、中部、出气口的孔道表面进行了 Raman 光谱测试。Ni/YSZ 电池和 Ba-Ni/YSZ 电池的 Raman 光谱结果存在差别。在入口、中部和出口位置, Ni/YSZ 电池燃料孔道表面均检测出 D 峰($1335\sim 1355 \text{ cm}^{-1}$)和 G 峰($1580\sim 1600 \text{ cm}^{-1}$),证实了在电池的入口、中部与出口的燃料孔道表面形成了积碳(见图6a)^[41];而改性电池的 Raman 测试没有出现 D 峰、G 峰,说明在改性电池燃料孔道的表面没有形成积碳,进一步证明通过在平管型 SOFC 阳极表面修饰 BaO 能够有效抑制积碳。

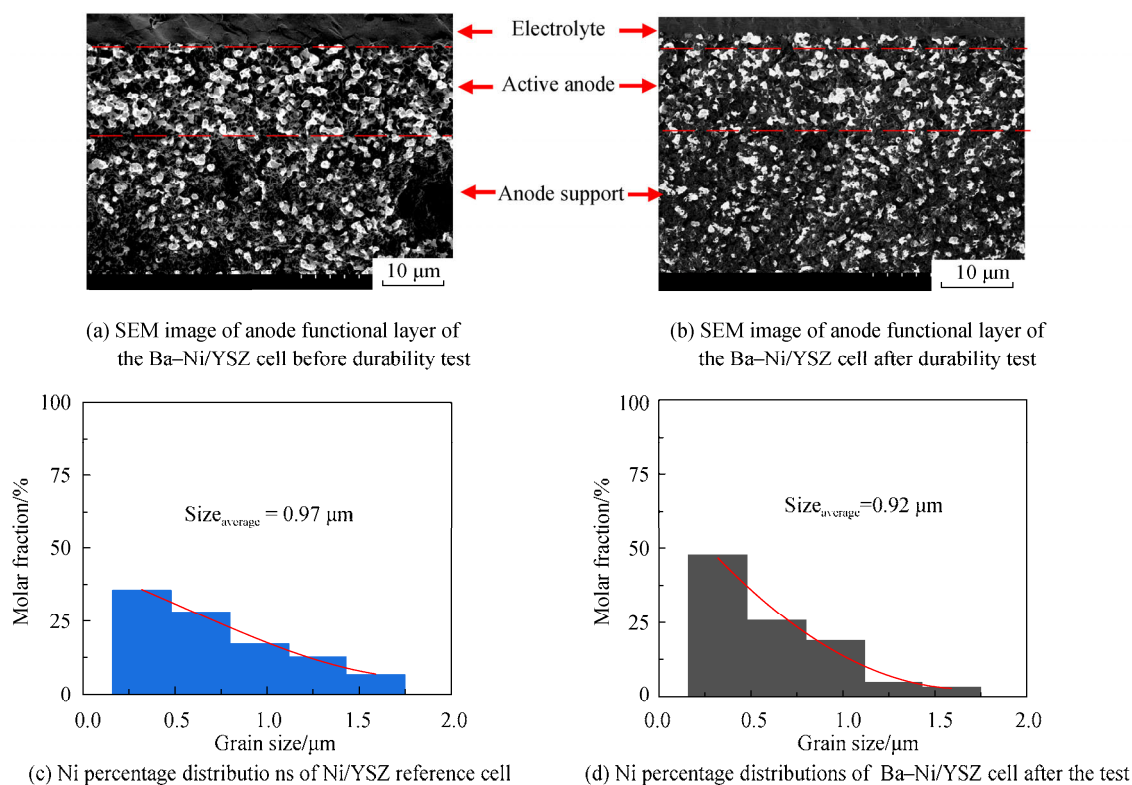


图 5 阳极功能层微观形貌与镍含量分析

Fig. 5 Microstructures of the anode functional layer and Ni pixel percentage analysis

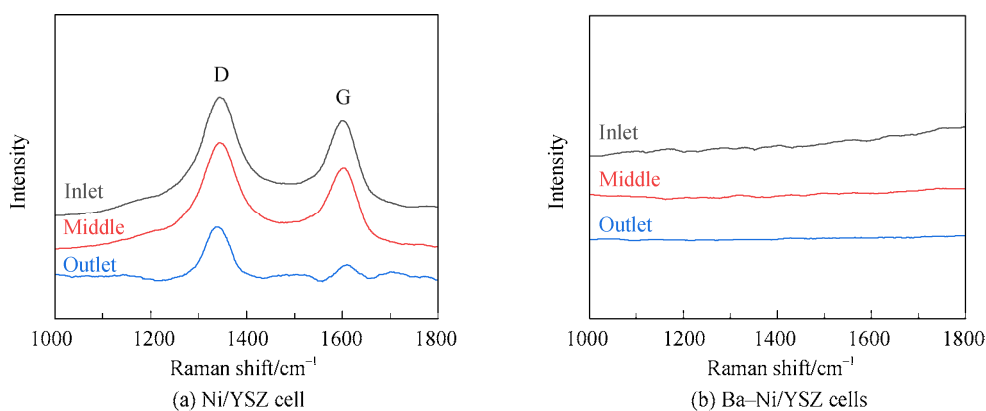


图 6 经耐久性测试后电池的 Raman 光谱

Fig. 6 Raman spectra of the cells after the durability test

3 结论

通过湿法浸渍对平管型 SOFC 的燃料通道表面进行 BaO 改性,提升电池的抗积碳性能。结果表明,在氢气气氛下, BaO 改性后对电池的输出功率无明显影响,但提升了甲醇气氛下的电池输出功率。在 750 °C, BaO 改性电池的甲醇转化率从 89.40% 提升至 92.70%。耐久性测试结果显示 BaO 改性电池的耐久性显著提升,实现在 750 °C, $r(S/C) = 0.75$ 条

件下 500 h 连续运行, Raman 光谱结果显示电池燃料孔道表面没有积碳产生。本工作表明阳极 BaO 改性能提高直接甲醇 SOFC 的输出功率、燃料转化率以及电池耐久性,为直接甲醇 SOFC 商业化应用提供了一种新的思路。

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Direct Methanol Operation on BaO Modified Anode in Flat-tube Solid Oxide Fuel Cells

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Extended abstract

Introduction The extensive use of fossil fuel resources has a serious impact on the environment, and hence energy conservation and CO₂ emission reduction have become the focuses of current development. Solid oxide fuel cells (SOFCs) have attracted the research attention because of the outstanding energy conversion efficiency, wide range of fuel choices, no pollution, and high quality waste. H₂ is the ideal fuel for SOFCs, but its low volumetric energy density and the requirement of high pressure to be liquefied, making it difficult to store and transport. At ambient temperature and pressure, methanol is liquid and its volumetric energy density is much higher than that of hydrogen, which makes methanol easy to storage and transport as a good hydrogen carrier. Furthermore, methanol has been quite mature production process. The industrial methanol production was hydrogenation of CO and CO₂. SOFCs can generate power with direct internal methanol reforming. However, the main problem of direct methanol fed SOFCs is carbon deposition. The formation of carbon deposition not only reduces the cell performance, but affects the anode structure as well. In this study, the anode surface of flat-tube anode supported SOFCs was modified by Barium. The cell performance, durability, and methanol conversion of the unmodified and modified SOFCs were compared and evaluated under methanol atmosphere with a steam/carbon ratio of 0.75.

Methods The anode support was composed of nickel oxide with 3%Y₂O₃-stabilized ZrO₂ (NiO–3YSZ, in mole), and the anode functional layer was made up of nickel oxide with 8%Y₂O₃-stabilized ZrO₂ (NiO–8YSZ). The electrolyte, barrier layer, and cathode layer were 8YSZ, Gd_{0.1}Ce_{0.9}O_{2-δ} (GDC), and La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ}-GDC (LSCF–GDC), respectively. The active cathode area was 60 cm². The cell is denoted as NiO–3YSZ|NiO–8YSZ|8YSZ|GDC|LSCF–GDC. Using 15.68 g Ba(NO₃)₂ powder dissolved in 200 mL deionized water, being stirred at 70 °C for 2 h, to obtain 0.3 mol/L barium nitrate precursor solution for wet impregnation. After sealing one end of the Ni/YSZ cell with wax, the prepared barium nitrate precursor solution (70 °C) was added into the fuel channels of through the sampler, and the other end of the cell was sealed with wax. The cell was kept in an oven at 50 °C for 24 hours to ensure that the Ba(NO₃)₂ solution was fully immersed in the anode channels. Then, the cell was dried at 90 °C for 1 h to remove the wax, and the cell obtained as above preparation processes was recorded as Ba–Ni /YSZ cell. After the cell was reduced at 750 °C by H₂, 0.60 L/min (SLM) H₂ was used as fuel for the initial cell performance test. When methanol was used as fuel for the test, the methanol solution with a steam/carbon ratio of 0.75 was added to the anode channels, and the temperature of the water steam generator was set at 130 °C. At this time, the corresponding methanol flow rate was 0.30 g/min, and 5 L/min air was passed into the cathode. Fuel cell testing equipment (SOFC-100W, Wuxi Lead Equipment Co., LTD.) and electro-chemical workstation (VMP3B-20, France BioLogic Co., LTD.) were used to test the electro-chemical performance and durability of the cell under different operating condition. The frequencies of electrochemical impedance spectroscopy (EIS) tests were ranging from 20 mHz to 30 kHz. The AC amplitude of EIS testing was 10 mV.

Results and discussion The scanning electrical microscopy (SEM) with energy dispersive spectrometer analysis proved that Ba element was effectively loaded on the surfaces of Ni/YSZ anode fuel channels. Under H₂ fuel, the current voltage (*I*–*V*) characteristics of Ni/YSZ and Ba–Ni/YSZ cells at 750 °C indicate that the open-circuit voltage (OCV) of Ni/YSZ and Ba–Ni /YSZ cells were 1.12 V and 1.07 V, respectively, which revealed that the cell air tightness was good. At 750 °C, the maximum power density (*P*_{max}) of Ni/YSZ and Ba–Ni/YSZ cells were 555.66 mW/cm² and 507.03 mW/cm², respectively, indicating that Ba element had no obvious influence on the cell output power of flat-tube SOFC fueled by H₂. The electro-chemical performance of Ni/YSZ and Ba–Ni/YSZ cells in methanol atmosphere [*r*(S/C) = 0.75] showed that the power density of Ni/YSZ and Ba–Ni/YSZ cells at 750 °C and 0.8V

were $326.72\text{mW}/\text{cm}^2$ and $452.87\text{mW}/\text{cm}^2$, respectively. It can be seen that the power density of Ba-modified cell was significantly improved when fueled by methanol. Under OCV condition, the methanol conversion rates of Ni/YSZ and Ba–Ni /YSZ cell were 89.40% and 92.70%, respectively, because Ba on the surfaces of the fuel channels promoted methanol conversion within the cell. The hydrophilicity of the Ba-modified cell was enhanced, and the water cracking into OH^- groups that were adsorbed on the Ni surface was promoted. The durability of Ni/YSZ and Ba–Ni/YSZ cells was tested at 750°C under methanol [$r(\text{S}/\text{C}) = 0.75$] and $200\text{ mA}/\text{cm}^2$. The results showed that the electro-chemical performance of Ni/YSZ cell deteriorated sharply shortly after 3 h to 4 h, while the voltage of Ba–Ni/YSZ cell kept stable. After running for more than 500 h, the OCV value of the Ba–Ni/YSZ cell remained stable, indicating that the air tightness of cell was good, and the voltage was 0.89 V with a deterioration rate of 0.01 (%) /h. The gas composition analysis of the Ba–Ni/YSZ cell during the durability test showed that the conversion rate of methanol in the modified cell during the test was stable, and the conversion rate was larger than 90%. According to the SEM images of the Ba–Ni/YSZ cell before and after the durability test, the average Ni particle size of anode functional layer of the Ba-modified cell lowered from $0.97\text{ }\mu\text{m}$ to $0.92\text{ }\mu\text{m}$. This deduced that the Ni particle lost in the anode function layer of the Ba–Ni/YSZ cell was obvious after the durability test, leading to the performance deterioration of the cell. Raman spectra showed that Ni/YSZ cell has detectable carbon deposition after the durability test, while Ba–Ni/YSZ has no carbon deposition. This showed that Ba content on the surface of the anode support of flat-tube SOFC could effectively inhibit carbon deposition.

Conclusions The performance and durability of the flat-tube Ba–Ni/YSZ cell were investigated in this study. The Ba–Ni/YSZ cell was prepared by wet impregnation. The power density of the Ba–Ni/YSZ cell with methanol under $r(\text{S}/\text{C})=0.75$ at 750°C was $452.87\text{ mW}\cdot\text{cm}^{-2}$ at 0.8 V, larger than that of Ni/YSZ cell. The durability of Ba–Ni/YSZ with methanol under $r(\text{S}/\text{C})=0.75$ at 750°C reached 500 h, while the Ni/YSZ cell revealed a sudden performance degradation. The Ni particle agglomeration was detected for the Ba–Ni/YSZ cell after the durability test, causing the performance degradation during the test. No carbon was observed on the surface of the Ba–Ni/YSZ after the durability test.

Keywords flat tube solid oxide fuel cell; zirconia; methanol; durability; carbon deposition