

地下煤气化合成气平管型固体氧化物燃料电池直接内重整发电特性

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摘 要: 以地下煤气化合成气为燃料, 研究了平管型固体氧化物燃料电池的直接内重整发电特性。结果显示以地下煤气化合成气(加拿大的 Swan Hills 煤矿区)模拟组分为燃气时, 在 750 °C 下电池的最大功率密度为 $361.9 \text{ mW} \cdot \text{cm}^{-2}$, 达到了相同状态下氢气燃料对应性能的 91.6%。在该燃料气氛下, 以 $300 \text{ mA} \cdot \text{cm}^{-2}$ 连续稳定运行 960 h, 电池的欧姆阻抗、极化阻抗分别由 0.108、 $0.485 \Omega \cdot \text{cm}^2$ 增大至 0.190、 $0.494 \Omega \cdot \text{cm}^2$, 对应增长率分别为 0.085、 $0.009 \Omega \cdot \text{cm}^2 \cdot \text{h}^{-1}$ 。Raman 光谱及微观结构分析结果显示, 电池性能的衰减主要是由燃料孔道表面的积碳、活性阳极层的镍颗粒团聚及镍含量损耗所致, 通过增加合成气中 CO_2 的含量可一定程度上抑制积碳, 提高电池运行稳定性。

关键词: 地下煤气化; 合成气; 稳定性; 固体氧化物燃料电池

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地下煤气化(UCG)技术对中国煤炭开发具有重要的意义, 日益受到关注^[1-3]。UCG 技术可直接在地下将煤炭转化成富含 CH_4 、 H_2 、 CO_2 、 CO 的合成气, 能够适应煤层深度大、煤层厚度小等价值低的煤炭资源开发, 极大降低了煤炭开采的经济成本、安全风险, 可大幅度提高煤炭开发的整体效率^[3-5]。基于 UCG 技术生产出的合成气可用于生产更高附加价值的化学用品, 如甲醇、氨、乙烯及费托合成产物, 也可用作供热、发电的燃料^[4, 6-7]。目前, 将 UCG 技术生产的合成气用于发电主要是通过内燃机进行, 能量转换效率受到 Carnot 循环限制, 通常约为 30%, 这与清洁、高效利用的目标相差甚远。固体氧化物燃料电池(SOFC)通过电化学反应将合成气燃料中的化学能直接转变成电能, 其发电效率可达 60%以上, 热电联供效率可达 90%, 不受 Carnot 循环的限制^[8-11]。因此, 如能利用 SOFC 进行 UCG 合成气发电, 对煤炭清洁开发、高效利用具有重要的意义。

近年来, 研究人员开展了一些有关合成气的 SOFC 研究^[12-16]。Chen 等^[12]以 Ni/氧化钇稳定氧化锆(YSZ)平板型阳极支撑电池(有效活性面积: 16

cm^2)为研究对象, 研究了其以合成气为燃料的发电特性, 结果显示在 750 °C 下, 电池以 $230 \text{ mA} \cdot \text{cm}^{-2}$ 运行, 2 h 后电池输出电压显著下降。Zhang 等^[17]报道了以 UCG 合成气为燃料的电解质支撑 SOFC(有效活性面积: 0.25 cm^2)性能, 结果显示在 750 °C 下, 电池的最大功率密度为 $235 \text{ mW} \cdot \text{cm}^{-2}$, 并在 0.7 V 工况下运行了 17 h, 具有一定的稳定性。Sang 等^[15]以平管型阳极支撑电池(有效活性面积: 60 cm^2)为研究对象, 以生物质合成气为燃料进行了研究, 结果显示在合成气中通入 5%(体积分数)水蒸气, 平管型结构电池实现了 800 h 无衰减的恒电流放电运行。Chen 等^[18]采用阳极支撑 SOFC(有效面积: 0.24 cm^2)进行研究, 通过在合成气中通入 CO_2 , 将合成气中 CH_4 重整成 H_2 与 CO , 同样延长了电池寿命。由于 UCG 合成气自身携带着一定含量的 CO_2 , 因此利用 UCG 合成气进行 SOFC 发电具有较大的潜力。

基于合成气为燃料的 SOFC 研究, 其主要对象包括平板型结构与平管型结构电池 2 大类。平板型 SOFC 因功率密度高而最受关注, 但以富含 CH_4 等组分的合成气为燃料时, 通常需要对燃料进行外重

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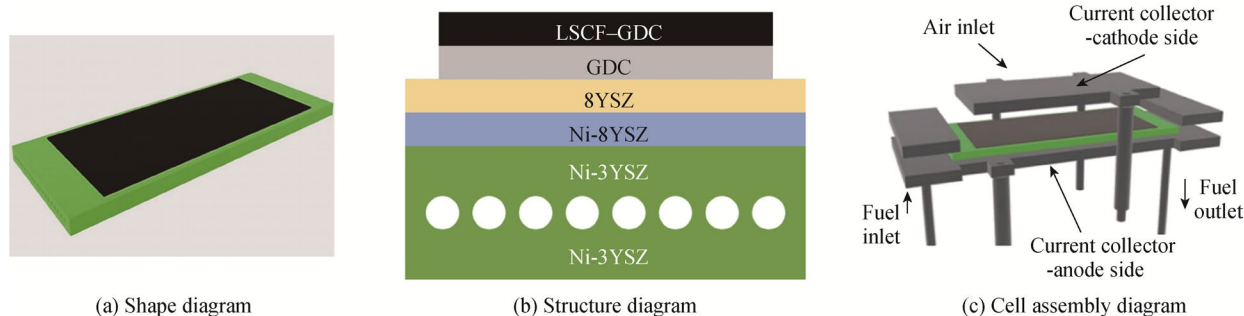
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整处理^[19], 这无疑会增加燃料使用的成本。相较于平板型结构 SOFC, 平管型 SOFC 功率密度略低, 但其具有的抗热冲击性能高、氧化还原循环稳定性强等特点使其具备了在严苛环境下使用的潜力^[11, 20–24]。本课题组对平管型结构电池在碳基燃料下的发电特性开展了系列研究, 结果显示平管型 SOFC 还具有较强的内重整与抗积碳特性^[21, 25], 这对以 UCG 合成气为燃料的高效利用可能更具有吸引力。本工作在已报道的工作基础上^[15, 21, 25], 采用 UCG 模拟合成气, 研究基于 UCG 合成气的平管型阳极支撑 SOFC 直接内重整放电特性, 并对其性能变化规律与作用因素进行分析, 为 UCG 合成气的清洁、高效利用提供参考。

1 实验

本研究采用平管型 Ni/YSZ 阳极支撑 SOFC, 电池的尺寸为 155.0 mm × 65.0 mm × 5.5 mm, 电池的有效活性面积为 60 cm², 电池示意结构如图 1a 所示。电池具体组成(图 1b)如下: NiO/3YSZ(阳极支撑层, 约 1.5 mm), NiO/8YSZ(活性阳极层, 15~20 μm), 8YSZ(电解质层, 15.0~20.0 μm), Gd_{0.1}Ce_{0.9}O_{2-δ} (GDC) (阻挡层, 约 1 μm), La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF)–GDC(阴极层, 15~20 μm)。3YSZ 和 8YSZ 分别为氧化钇掺杂量为 3%(摩尔分数, 下同)的 YSZ 和氧化钇掺杂量为 8%的 YSZ。



LSCF: La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ}; GDC: Gd_{0.1}Ce_{0.9}O_{2-δ}.

图 1 平管型固体氧化物燃料电池(SOFC)的外观、结构与装配示意图

Fig. 1 Schematic images of a flat-tube solid oxide fuel cell (SOFC): Shape, structure, and cell assembly

2 结果与讨论

2.1 UCG 合成气模拟气的直接内重整发电特性

表 1 为国际上几种主要的 UCG 合成气的成分^[4, 27–28], 显然可以看到不同地区的 UCG 合成气组分差异较大。本工作首先采用 Gibbs 自由能最小化法^[25], 通过 HSC Chemistry 6 (Outoumpu, Finland) 对不同地区的 UCG 合成气热力学积碳可

电池阳极支撑体通过挤出成型制备而成, 活性阳极、电解质、阻挡层、活性阴极则通过丝网印刷和烧结工艺制备而成^[21]。制备后的电池按照如图 1c 所示的结构进行封装^[15, 25]。安装完成后, 将电池放于电炉中加热到 750 °C 后, 进行保温测试。测试过程中, 首先在阳极侧通入 0.3 L·min⁻¹ 氢气进行还原, 同时在阴极侧通入 1.0 L·min⁻¹ 空气。还原约 4 h 后, 电池阳极被完全还原, 此时开路电压(OCV)处于稳定, 可开始进行电化学性能测试。

电池的电化学性能测试主要包括: OCV、电流–电压(*I*–*V*)极化曲线、电化学阻抗(EIS), 其中 OCV、*I*–*V* 极化曲线通过电化学测试设备(100 W, 浙江氢邦科技有限公司, 中国)进行检测, 电化学阻抗通过电化学工作站(VMP3B-20, Bio Logic, 法国)进行测试记录, 测试频率 30 mHz 到 30 kHz, 交流振幅为 10 mV。为了分析影响电池性能的因素, 采用弛豫时间分布(DRT)方法进一步对电池阻抗进行分析^[25–26]。

为了分析电池的直接内重整效果, 采用气相色谱仪(GC-7820, 山东鲁南分析仪器有限公司, 中国)对以合成气模拟气为燃料测试过程中收集的电池阳极尾气组分进行分析。采用扫描电子显微镜(SEM, S4800, Hitachi, 日本)对测试后的电池微观进行表征, 采用 Raman 光谱仪(inVia Reflex, Renishaw, 英国)对电池阳极侧的碳沉积形式进行分析。

能性进行分析, 结果如图 2a 所示。由图 2a 可见, 在 SOFC 工况下, 随着温度升高, 各类合成气积碳倾向在减弱, 特别是在 750 °C 下, 表 1 中大部分合成气都不易于形成积碳。图 2b 为不同 CO₂ 含量下的 UCG 合成气(加拿大的 Swan Hills 煤矿区)的积碳预测, 结果表明, 当固定 H₂、CO、CH₄、CO₂ 组分的流量时, N₂ 的含量不影响积碳倾向, 增加 CO₂ 含量有助于抑制积碳。

图 3 为通入表 1 中显示的各类 UCG 模拟合成气(流量固定为 $0.6 \text{ L} \cdot \text{min}^{-1}$, 且不考虑 N_2 稀释)时平管型 SOFC 在 750°C 下的放电性能。由图 3 可见, 当在 0.8 V 下通入 H_2 时, 输出功率密度为 $260.3 \text{ mW} \cdot \text{cm}^{-2}$, 最大输出功率密度为 $395.1 \text{ mW} \cdot \text{cm}^{-2}$; 当通入同等当量 H_2 的 UCG 合成气时, 以 UCG 合成气(Swan Hills)为例, 结果显示电池在 0.8 V 下的输出功率密度为 $240.1 \text{ mW} \cdot \text{cm}^{-2}$, 最大输出功率密度为 $361.9 \text{ mW} \cdot \text{cm}^{-2}$, 达到 H_2 燃料对应下的 91.6%。从

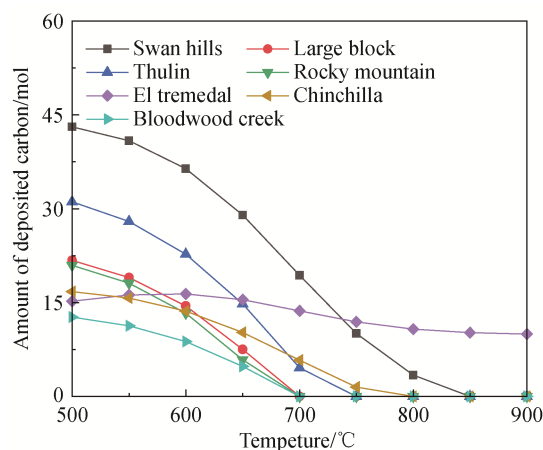
图 3 中结果可知, 表 1 所示的其它几种 UCG 合成气的输出功率密度均小于 Swan Hills 的 UCG 合成气, 并且其它几种合成气含大量 N_2 , 造成燃料的稀释, 从而进一步降低电池的性能。然而, 结合图 2 所示的热力学积碳预测结果可以发现, UCG 合成气(Swan Hills)在 750°C 更容易形成积碳。因此, 为了便于研究因积碳导致的 SOFC 性能衰减, 及由此提出抑制积碳的策略, 本工作选取 UCG 合成气(Swan Hills, 下同)为研究对象开展长期稳定性测试。

表 1 典型的地下煤气化(UCG)合成气信息

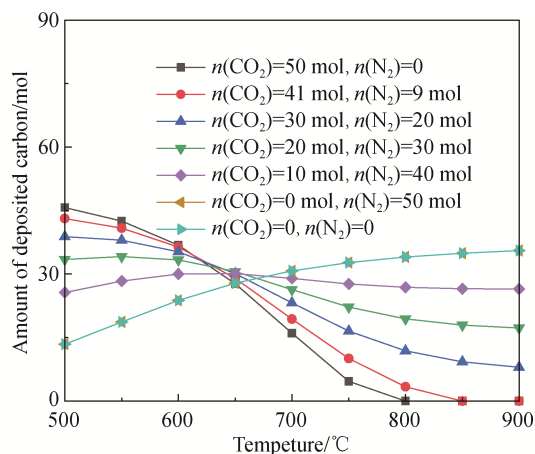
Table 1 Information about the typical underground coal gasification (UCG) syngas

Types of UCG syngas	Composition (volume fraction, ϕ)/%					LHV/ ($\text{MJ} \cdot \text{Nm}^{-3}$)	Depth/m	Reference
	H_2	CO	CO_2	CH_4	N_2			
Swan Hills	15.3	5.1	41.8	37.8	100.0	16.0	1 400	[4, 27]
Rocky Mountain	40.0	12.0	37.0	9.0	2.0	9.5	110	[4, 28]
Bloodwood Creek Panel	21.2	2.6	22.0	8.7	45.4	5.7	200	[4]
Chinchilla	20.0	10.0	15.0	10.0	45.0	5.0	130	[4, 28]
E1 Tremedal	39.1	20.3	5.8	20.3	14.5	10.9	550	[4]
Thulin	6.6	1.3	60.5	31.6		12.4	860	[4]
Large Block Experiment	42.5	25.3	28.3	3.5	0.4	8.5–9.5	NR	[4]

Note: LHV represents lower heating value; NR is not reported.



(a) Different underground coal gasification technology (UCG) syngas, $n(\text{fuel})=100 \text{ mol}$ (n is in mole)



(b) UCG syngas (Swan Hills) with different compositions of CO_2 ; $n(\text{CH}_4)=37 \text{ mol}$, $n(\text{H}_2)=15 \text{ mol}$, $n(\text{CO})=5 \text{ mol}$

n is in mole.

图 2 基于热力学计算的积碳与温度关系

Fig. 2 Amount of deposited carbon under different temperatures based on thermodynamic calculations

图 4 为 750°C 下以 UCG 合成气为燃料的稳定性测试结果, 测试过程中分别通入不同含量的 CO_2 气体(具体组分构成如表 2 所示), 其中恒定电流密度为 $300 \text{ mA} \cdot \text{cm}^{-2}$ 。在通入不同含量 CO_2 气体时, 始终保持 UCG 合成气原有 H_2 、 CO 、 CH_4 体积分数的比例固定不变, 为此以 N_2 来保持总气量的平衡。如表 2 所示, 以燃料气体组分变化为依据将稳定性测试分成 7 个阶段, CO_2 气体含量从高到低分别定义为阶段 1、2、3、4、5、6 和 7。

由图 4a 可见, 当 CO_2 含量高于或等于 20%(体积分数, 下同)时, 衰减率在各阶段均小于 2.7%每 100 h, 且无性能突降, 表明该条件下平管型 SOFC 可稳定运行。由于 UCG 合成气原始成分与阶段 2(112~214 h)相近, 这说明平管型 SOFC 能够直接以 UCG 合成气为燃气进行稳定发电。当电池运行至 460 h 时, 将 CO_2 含量降至 10%, 电压在 520 h 时发生剧烈波动, 随后 CO_2 继续下降至 0 时, 电池继续稳定运行 144 h, 然而当电池在运行至 750 h 关闭 N_2

后, 则电池性能衰减显著。

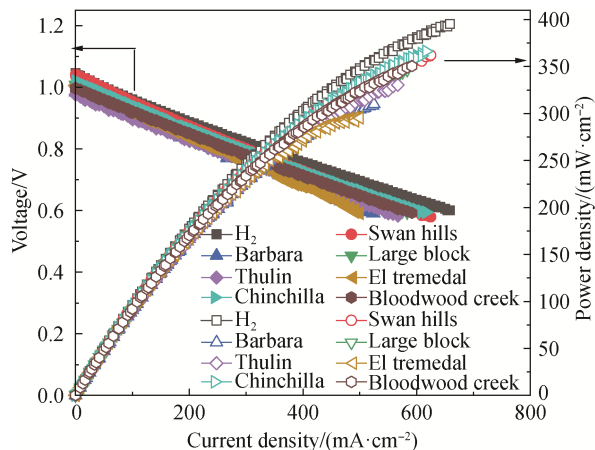


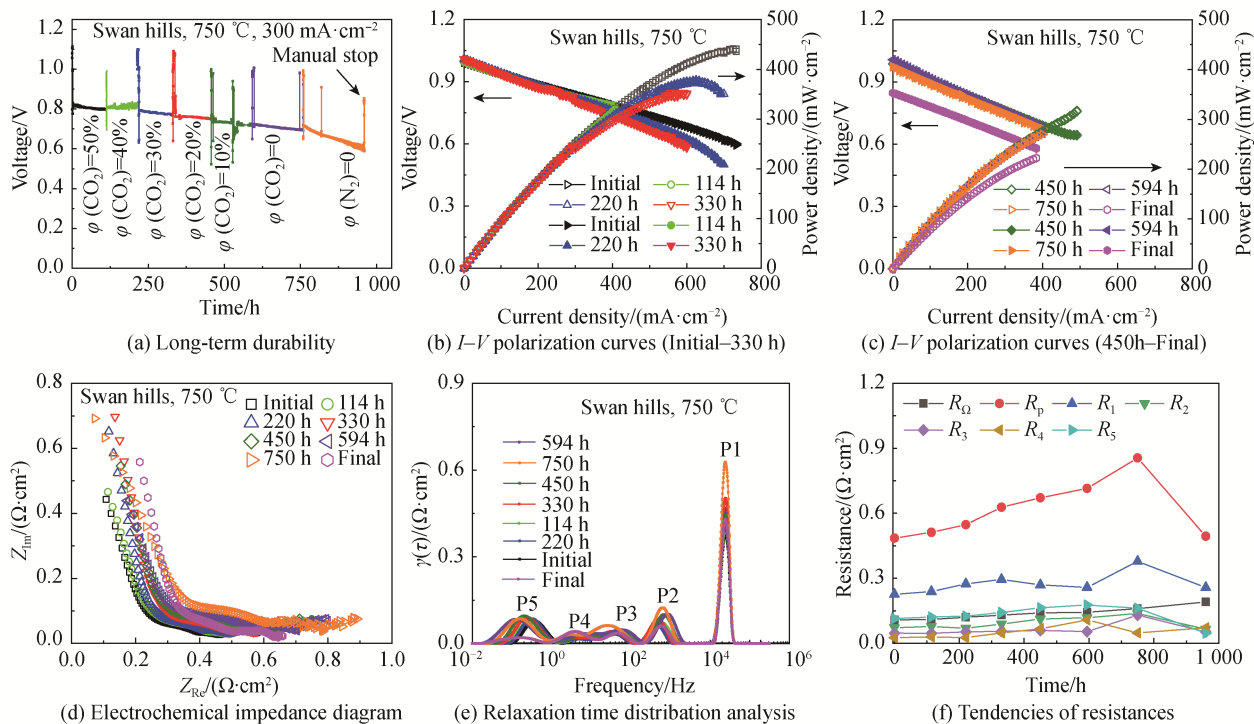
图3 平管型 SOFC 在 750 °C 下使用不同 UCG 合成气作为燃料的 I - V 极化曲线

Fig. 3 I - V polarization curves of flat-tube SOFC under different UCG syngases at 750 °C

图 4b 和图 4c 为不同运行时间段下的 I - V 曲线, 在前 750 h (阶段 1 至阶段 7), 电池 OCV 较为稳定, 表明平管型 SOFC 电池结构完整。当电池运行至 960 h 终止实验时, 电池 OCV 显著下降到 0.845 V, 表明电池在阶段 7 (750~960 h) 期间可能出现了微裂纹, 导致阳极燃料泄露, 阳极侧氧分压上升, 使得 OCV 下降^[21], 该微裂纹是由于阶段 7 期间, 关闭

N_2 后积碳更加严重导致。根据表 2 数据可计算获得电池运行各阶段的气体分压。本实验的电池在阶段 7 运行期间, H_2 、 CO 、 CH_4 的分压分别从阶段 6 (591~750 h) 的 0.132、0.044、0.324 提高到了 0.264、0.088、0.648。气体分压增大后, 单位体积内分子间碰撞频率大幅增加, 从而提高了形成积碳反应的概率, 加大了电池性能的衰减, 这是阶段 6、阶段 7 中电池性能衰减率差别(衰减率: 阶段 6 小于阶段 7)的主要原因, 由此可推断出, N_2 的稀释作用能够有效减缓电池内部的积碳形成。

图 4d 为测试各阶段对应的 EIS 曲线。随着测试的进行, EIS 曲线逐步向右平移, 即阻抗逐步增大。采用文献[25–26, 29–30]报道的方法, 对阻抗进行 DRT 分析, 图 4e 中有 5 个可识别的峰 (P1~P5), 其对应的电极过程分别是^[25–26, 29–30]: P1 峰($10^3 \sim 10^4$ Hz)关联于离子传输及阳极电荷转移过程; P2 峰($\approx 10^3$ Hz)对应于阳极三相界面附近气体扩散过程; P3 峰($\approx 10^2$ Hz)与氧气在 LSCF 表面吸附过程及在 LSCF 阴极内氧离子扩散过程有关; P4 峰(≈ 10 Hz)与 P5 峰(≈ 1 Hz)分别关联于气体在 Ni/YSZ 阳极支撑体内部与燃料孔道内扩散过程。P4、P5 峰强度与电池阳极侧的氧分压呈负相关^[15, 31]。



Z_{im} : Imaginary part of the impedance; Z_{Re} : Real part of the impedance; τ : Relaxation time; $\gamma(\tau)$: Characteristics of relaxation time distribution; R_Ω , R_p , R_1 , R_2 , R_3 , R_4 , and R_5 are the ohmic resistance, polarization resistance, and the resistance of P1, P2, P3, P4, and P5, respectively.

图4 以 UCG 合成气 (Swan Hills) 为燃料的平管型 SOFC 耐久性测试

Fig. 4 Long-term durability test of flat-tube SOFC fueled with UCG syngas (Swan Hills)

图 4f 为通过拟合图 4d 和图 4e 获得的每部分阻抗变化规律。 R_1 、 R_2 、 R_3 、 R_4 、 R_5 分别为 P1、P2、P3、P4、P5 峰对应的阻抗。由图 4f 可见, 欧姆阻抗 R_Ω 逐渐增加, 但增加幅度较小, 而极化阻抗 R_p 在前 750 h 逐步增大, 且增长逐渐加快, 其中主要影响来自于 R_1 、 R_4 和 R_5 , 这说明阳极侧离子、电荷传输过程及燃料在燃料孔道内、阳极支撑体内部的扩散过程受到影响。此外, R_4 和 R_5 的强度增加较明显, 说明积碳对燃料孔道、阳极支撑体内气体扩散影响较大。在阶段 7 (750~960 h), R_p 突然降低。结合图 4b 和图 4c 中 OCV 在这个运行阶段, 由 0.973 V (750 h) 下降至 0.845 V (960 h), 可以推测出电池在这个阶段出现微裂纹, 导致阳极燃料气泄漏, 阳极侧氧分压上升, 进而使 R_4 、 R_5 和 R_p 减小^[15, 32]。由于平管型 SOFC 具有较大的有效面积 (60 cm²) 与较高的机械强度^[21], 即使可能出现了微裂纹, 电池直至最后依然能够维持一定的性能。 R_3 在 0~960 h 保持相对稳定, 说明电池阴极性能保持稳定, 对电池整体性能衰减的影响较小。经 960 h 运行后, R_Ω 和 R_p 分别由 0.108、0.485 $\Omega \cdot \text{cm}^2$ 增大至 0.190、0.494 $\Omega \cdot \text{cm}^2$, 增长率分别为 0.085 $\Omega \cdot \text{cm}^2 \cdot \text{kh}^{-1}$ 和 0.009 $\Omega \cdot \text{cm}^2 \cdot \text{kh}^{-1}$ 。

表 2 平管型 SOFC 长期稳定性测试中不同阶段所使用的 UCG 合成气(Swan Hills)组分

Table 2 Gas compositions of UCG syngas (Swan Hills) used for the flat-tube SOFC in the different stages during the long-term test

Stage	$\varphi(\text{H}_2)/\%$	$\varphi(\text{CO})/\%$	$\varphi(\text{CH}_4)/\%$	$\varphi(\text{CO}_2)/\%$	$\varphi(\text{N}_2)/\%$
Stage 1	13.2	4.4	32.4	50.0	0
Stage 2	13.2	4.4	32.4	40.0	10.0
Stage 3	13.2	4.4	32.4	30.0	20.0
Stage 4	13.2	4.4	32.4	20.0	30.0
Stage 5	13.2	4.4	32.4	10.0	40.0
Stage 6	13.2	4.4	32.4	0	50.0
Stage 7	26.4	8.8	64.8	0	0

2.2 电池性能衰减因素分析

对测试后的电池燃料孔道表面积碳情况进行 Raman 光谱分析, 结果如图 5 所示, 电池经过 960 h 运行后, Raman 光谱中出现了 2 个积碳的特征峰: D 峰 (1 335~1 350 cm⁻¹) 与 G 峰 (1 580~1 600 cm⁻¹), 表明在电池燃料孔道的表面有积碳形成^[21]。当积碳

的石墨化程度(结晶度)较大时, 积碳的晶格结构较完整, 晶格缺陷较少。 I_D/I_G (D 峰、G 峰强度比) 能反映积碳的结晶度, 比值越高, 结晶度越低, 积碳形成过程越迅速^[21]。以 UCG 合成气为燃料电池的 I_D/I_G 比值是 1.57, 该比值小于文献[21]的报道, 说明 UCG 合成气在电池中积碳结晶度较高, 积碳形成过程较平缓。

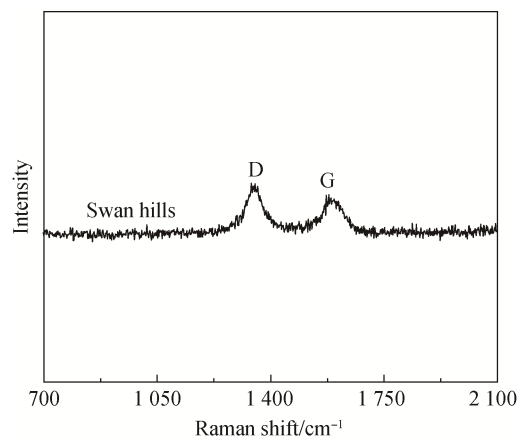


图 5 经过长期测试后电池的 Raman 光谱结果

Fig. 5 Raman spectroscopy analysis of the cells after long-term test

通过 SEM 表征了电池活性阳极层及其附近的形貌变化。由图 6 可见, 灰色暗区、白色亮区分别是 YSZ 相、Ni 相^[25]。图 6a 为对照电池(氢还原后的电池)的形貌, 镍颗粒均匀分布在活性阳极层(距离电解质层 0~15 μm) 与活性阳极层附近(距离电解质层 15~45 μm)。图 6b 是在 UCG 合成气气氛下经长期测试后的电池活性阳极附近区域的形貌。通过 ImageJ 对图 6a 和图 6b 进行分析, 获得活性阳极层及其附近的 Ni 颗粒大小分布(图 6c)与 Ni 含量分布(图 6d)。由图 6c 可见, 对照电池中小尺寸 Ni 颗粒更多, 平均 Ni 颗粒粒径大小排序: UCG 合成气电池 (1.189 μm) > 对照电池 (1.016 μm), 表明经过 960 h 发电后, UCG 合成气电池发生显著的 Ni 颗粒团聚, 平均 Ni 颗粒粒径增长 17.0%。

图 6d 显示经过长期测试后, 电池出现了 Ni 含量损失, 尤其是其靠近电解质层附近 (0~5 μm) 的 Ni 含量由 30.0% (像素, 下同) 下降至 19.2 %。根据文献[33]报道可知, Ni 颗粒团聚、Ni 含量损失是响 R_Ω 增大及性能衰减(图 4a 和图 4c)的主要因素。

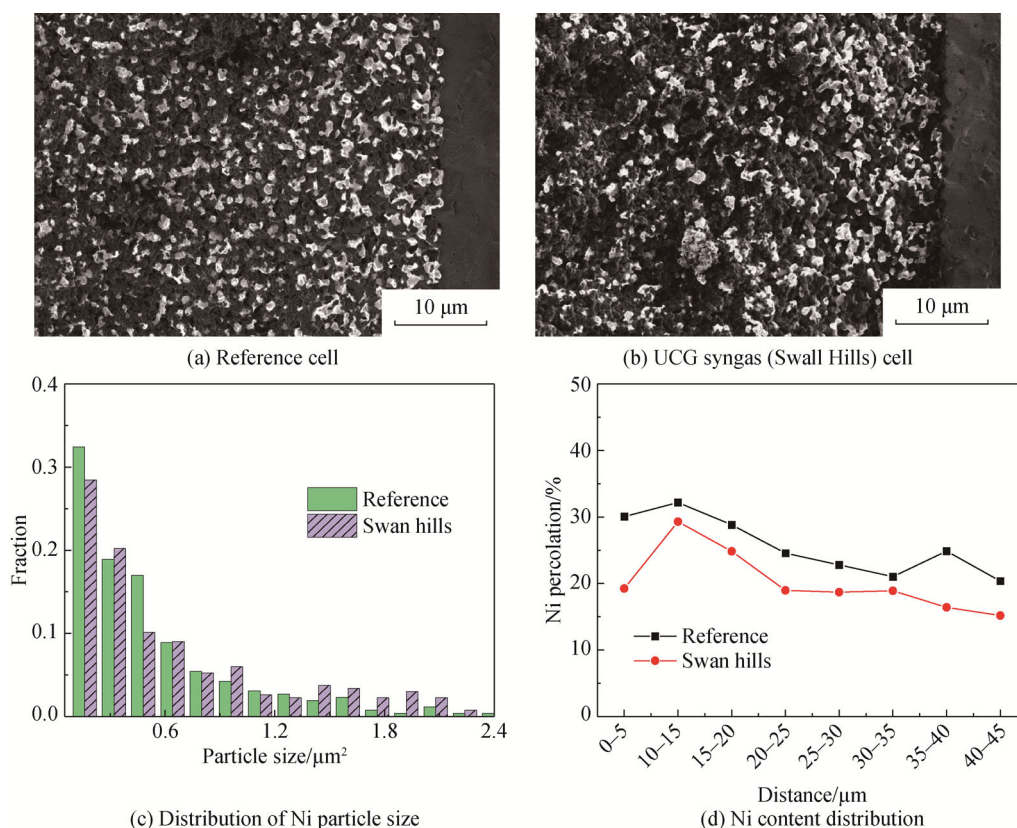


图6 活性阳极层及其附近的微观形貌
Fig. 6 Micro-morphologies of the cells near the anode functional layer

3 结论

本工作研究了基于 UCG 合成气的平管型 SOFC 直接内重整发电性能,并分析了其作用因素与机理,结果显示当以 UCG 合成气(Swan Hills)为燃气时,平管型 SOFC 的输出功率密度在 750 °C 下接近氢气气氛下的输出功率密度性能,以 $300 \text{ mA} \cdot \text{cm}^{-2}$ 稳定运行了 960 h,电池对应的 R_{Ω} 、 R_p 分别由 0.108、 $0.485 \Omega \cdot \text{cm}^2$ 增大至 0.190、 $0.494 \Omega \cdot \text{cm}^2$ 。显然,平管型 SOFC 对 UCG 合成气具有可直接内重整稳定运行的适应性。通过通入不同含量 CO_2 气体调节 UCG(Swan Hills)气体组分,电池具有不同的衰减性能。Raman 光谱结果显示在燃料孔道的表面形成了一定程度的积碳。SEM 结果显示活性阳极层中平均 Ni 颗粒粒径增长 17.0%,且靠近电解质(0~5 μm)的阳极功能层中 Ni 含量下降了 10.8%(像素)。燃料孔道表面的积碳、活性阳极层的 Ni 颗粒团聚及 Ni 含量损失是电池性能衰减的主要原因。通过调控 UCG 合成气中的 CO_2 气体比例,平管型 SOFC 能够实现 UCG 合成气燃料直接内重整的长期稳定运行,为煤炭的清洁开发与高效利用提供了新思路。

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Power Generation via Flat-Tube Solid Oxide Fuel Cells by Direct Internal Reforming of Syngas from Underground Coal Gasification

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Extended Abstract

Introduction Underground coal gasification (UCG) technology is critical to coal development in China, which has attracted recent attention. UCG technology can directly convert coal into syngas rich in CH₄, H₂, CO₂, and CO beneath the earth surface, which is appropriate for the employment of coal resources with a low value (*i.e.*, coal resources in large depths or with restricted thickness). UCG technology significantly reduces the economic cost and safety risks of coal mining and improves the overall efficiency of coal

utilization. Syngas obtained from UCG technology is used to produce higher-value-added chemicals, such as methanol, ammonia, ethylene, and Fischer-Tropsch synthesis products, and the fuel for heating and power generation. Using syngas produced by UCG technology for power generation is mainly carried out through internal combustion engines. The energy conversion efficiency is limited by the Carnot cycle, usually about 30%, which diverges from the goal of clean and efficient use. Solid oxide fuel cells (SOFCs) convert the chemical energy in syngas fuel directly into electrical energy through electrochemical reactions. The conversion efficiency is considerably high and is not limited by the Carnot cycle. Power generation efficiency of > 60% and combined heat and power (CHP) efficiency of > 90% can be achieved. Therefore, SOFCs can efficiently employ the syngas from UCG, which is important for the clean and efficient development and utilization of coal. Flat-tube SOFCs exhibit high thermal shock resistance and stability under the redox cycle and are capable of being used in harsh environments. This paper was to investigate power generation using flat-tube SOFCs fed with carbon-containing fuels. In addition, the performance and durability of anode-supported flat-tube SOFCs with direct internal reforming of syngas from UCG were also analyzed.

Methods The flat-tube Ni/yttria-stabilized zirconia (YSZ) anode-supported cell contains a porous NiO–3YSZ (3% yttria-stabilized zirconia, in mole fraction, ~1 mm thick) anode support, a NiO–8YSZ (8% yttria-stabilized zirconia, in mole fraction, 15–20 μm thick) anode functional layer, a dense 8YSZ electrolyte layer (15–20 μm thick), a gadolinia-doped ceria (GDC) barrier layer (~3 μm thick), and a porous $(\text{La}_{0.6}, \text{Sr}_{0.4})(\text{Co}_{0.2}, \text{Fe}_{0.8})\text{O}_3$ (LSCF)–GDC cathode layer (15–20 μm thick). The cell was indicated as NiO–3YSZ|NiO–8YSZ|8YSZ|GDC|LSCF–GDC. The cell dimensions were 155 mm $\times$ 65 mm $\times$ 5.5 mm with an active cathode area of 60 cm^2 . The cell was heated in air at 750 $^{\circ}\text{C}$ after assembly. The anode was reduced under 0.3 $\text{L}\cdot\text{min}^{-1}$ H_2 prior to the electrochemical tests. H_2 or syngas was fed to the anode to evaluate the cell performance. To evaluate the electrochemical cell performance, the open-circuit voltage (OCV), current-voltage (I – V) characteristics, and electrochemical impedance under different conditions were measured by a model VMP3B-20 electrochemical workstation (BioLogic Co., France). The electrochemical impedance spectra (EIS) were recorded under OCV condition in the frequency range of 30 mHz to 30 kHz at an alternating current of 10 mV.

Results and discussion The increasing temperature reduces a carbon deposition in SOFC fueled with different syngas. Especially at 750 $^{\circ}\text{C}$, the carbon deposition is not favorable for most types of UCG syngas. When the flow rates of H_2 , CO, CH_4 , and CO_2 are fixed, the composition of N_2 does not affect the carbon deposition. Increasing the composition of CO_2 mitigates the carbon deposition. The power density of SOFC with H_2 at 750 $^{\circ}\text{C}$ is 260.3 $\text{mW}\cdot\text{cm}^{-2}$ at 0.8 V, and the maximum power density is 395.1 $\text{mW}\cdot\text{cm}^{-2}$. The power density of a cell fueled with syngas (Swan Hills) at 0.8 V is 240.1 $\text{mW}\cdot\text{cm}^{-2}$, and the maximum power density is 361.9 $\text{mW}\cdot\text{cm}^{-2}$, reaching 91.6% of that with H_2 . The power densities of SOFC fueled with other types of UCG syngas are lower than those fueled with syngas (Swan Hills). The stability test of the flat-tube SOFCs fed with syngas (Swan Hills) is conducted at 750 $^{\circ}\text{C}$ under 300 $\text{mA}\cdot\text{cm}^{-2}$. During the test, the composition of CO_2 is changed. The flat-tube SOFC can discharge stably for 960 h. When the CO_2 content is higher than or equal to 20% (in volume fraction), the degradation rate is less than 2.7% every 100 h in each stage. No sudden performance degradation emerges, indicating that the flat-tube SOFCs can run stably under such conditions. Since the original composition of syngas (Swan Hills) is similar to that of stage 2 (for 112–214 h), a stable power generation from flat-tube SOFCs directly using UCG syngas (Swan Hills) is viable. The CO_2 content reduces to 10% at approximately 460 h. The voltage fluctuates sharply at 520 h. Subsequently, when CO_2 further decreases to 0, the cell operates stably for another 144 h. However, when N_2 flow is stopped at 750 h, the performance deteriorates significantly. After the long-term test, two characteristic peaks of carbon deposition appear in the Raman spectrum, *i.e.*, the D peak (at 1335–1350 cm^{-1}) and the G peak (at 1580–1600 cm^{-1}). The result indicates that the carbon deposition is formed on the surfaces of the fuel channels. The SEM images show that after the test at 960 h, a significant Ni particle agglomeration occurs in the active anode layer of the cell fed with syngas (Swan Hills), and the average Ni particle size is increased by 17.0%. The Ni content loss in the active anode layer appears. Especially, the Ni content near the electrolyte layer (0–5 μm) decreases from 30.0% (pixel, same below) to 19.2%. Carbon deposition, nickel agglomeration, and nickel particle loss result in a performance degradation.

Conclusions The cell performance and durability of flat-tube solid oxide fuel cells by direct internal reforming of syngas from underground coal gasification were investigated. The peak power density of the cell with syngas (Swan Hills) from underground coal gasification was 361.9 $\text{mW}\cdot\text{cm}^{-2}$ at 750 $^{\circ}\text{C}$ (Note: Swan Hills is a coal mine in Canada), which was approximately 91.6% of that with H_2 . A stable operation with a constant current of 300 $\text{mA}\cdot\text{cm}^{-2}$ at > 960 h was realized. The ohmic resistance and polarization resistance increased from 0.108 $\Omega\cdot\text{cm}^2$ and 0.485 $\Omega\cdot\text{cm}^2$ to 0.190 $\Omega\cdot\text{cm}^2$ and 0.494 $\Omega\cdot\text{cm}^2$, respectively. The increased rates of the ohmic resistance and polarization were 0.085 $\Omega\cdot\text{cm}^2\cdot\text{h}^{-1}$ and 0.009 $\Omega\cdot\text{cm}^2\cdot\text{h}^{-1}$, respectively. The main degradation mechanisms were the carbon deposition on the anode, Ni percolation loss, and Ni particle agglomeration, detected by Raman spectroscopy and scanning electron microscopy. Elevating CO_2 concentration suppressed the carbon deposition, improving the cell stability.

Keywords underground coal gasification; syngas; stability; solid oxide fuel cell