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Fabrication and Characterization of the Ni-ScSZ Composite Anodes with a LSCM-CeO_2 Catalyst Layer in Thin Film SOFC

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固体氧化物燃料电池 LSCM–CeO_2/Ni–ScSZ 复合阳极制备及性能表征

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摘要: 采用双层流延法制备 Ni–ScSZ 阳极支撑层–ScSZ 电解质复合膜. 在烧结的 Ni–ScSZ 阳极支撑层表面丝网印刷一层 LSCM–CeO_2 阳极催化层,得到 LSCM–CeO_2/Ni–ScSZ 功能梯度层阳极. 研究表明,LSCM/CeO_2 比为 1∶3 (by mass)的功能梯度层阳极 Ni–ScSZ13 具有较佳的性能. 单电池在 850 ℃以 H_2 和乙醇蒸气作燃料的最大功率密度分别为 710 和 669 mW/cm^2,而 LSCM/CeO_2 为 1∶0(by mass)的功能梯度层 Ni–ScSZ10 作阳极的单电池,最大功率密度分别为 521 和 486 mW/cm^2. 两种阳极单电池,分别在 700 ℃于乙醇蒸气中作长时间运行实验,X–射线能量散射分析表明 Ni–ScSZ13 阳极比 Ni–ScSZ10 阳极具有较好的抗碳沉积性能.

关键词: 电化学性能; 碳沉积; 催化层; 交流阻抗; 固体氧化物燃料电池(SOFC)
中图分类号: TM911 **文献标识码:** A

固体氧化物燃料电池(SOFC)阳极系统主要有:Ni–YSZ 加水蒸气[1],氧化铈系[2-4],钙钛矿型结构氧化物系[5-8],Cu–YSZ 系[9-11],其它结构类型或非标准钙钛矿型结构的电子导体氧化物系[12-15]. 其中,Ni–YSZ 金属陶瓷阳极,若以甲烷作燃料,必须严格控制 CH_4/H_2O 比,该阳极可以有效地催化甲烷的内重整反应,避免碳沉积. 但内重整反应会造成电解质–电极"三合一"组件温度分布严重不均,进而导致电极剥离或组件脆裂,影响 SOFC 的安全稳定运行. 氧化铈在中温下电子导电率和催化活性均不高,需引入 Ni 金属. 而 Cu–YSZ 系,因浸入的金属量不多,电子导电率低,而钙钛矿结构的陶瓷基阳极(如掺杂的 $LaCrO_3$ 和 $SrTiO_3$)虽抗碳沉积性能优良,但活性差.

本文于烧结的 Ni–ScSZ 阳极支撑层表面丝网印刷一层 $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_3$–$CeO_2$ 催化层,组成功能梯度层阳极,以氢或乙醇蒸气(80 ℃水浴)为燃料,氧气为氧化剂,研究 LSCM–CeO_2/Ni–ScSZ 阳极的 SOFC 单电池的性能.

1 单体电池与测试

阳极:以乙醇和丁酮的共沸物作溶剂,将氧化钪稳定的氧化锆(ScSZ)或 50% (by mass) NiO–50% (by mass) ScSZ,粘结剂(PVB:10% ~15%),分散剂(三乙醇胺:2% ~3%),造孔剂(草酸氨:10% ~15%)和增塑剂(聚乙二醇:6% ~9%)混合,球磨 4 h 制浆,二次流延制得 Ni–ScSZ 支撑体–ScSZ 电解质复合膜,静压,脱脂烧结 1400 ℃ 3 h,得到复合膜(Φ14 mm).

低温燃烧法合成 $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_3$ (LSCM),加 CeO_2 与松油醇混合成浆料,经丝网印刷沉积到阳极支撑层 Ni–ScSZ 上,1100 ℃烧结 2 h 成 LSCM–CeO_2/Ni–ScSZ 功能梯度层. LSCM/CeO_2 (by mass)分别取为 1∶0、1∶1 以及 1∶3,简记为 Ni–ScSZ10、Ni–ScSZ11 以及 Ni–ScSZ13.

阴极:将固相合成的$(Pr_{0.7}Ca_{0.3})_{0.9}MnO_3$,与松油醇混合制浆,经丝网印刷沉积到电解质 ScSZ 上,1200 ℃烧结 2 h 制成 PCM,组合构成 Ni–ScSZ/ScSZ/PCM 单体半电池.

单体电池:将由阳极、阴极及催化层组成的 Ni–ScSZ/ScSZ/PCM 单电池密封于 Al_2O_3 管的一端,管内通 H_2 或乙醇蒸气,管外通 O_2,使用 IM6e 电化学工作站(Zahner–Elektrik GmbH FRG,Germa–

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ny)测试电池的 $V \sim I$ 曲线及交流阻抗谱图. 扫描电子显微镜(SEM,Philips515 型)观察样品形貌.

2　结果与讨论

2.1　单体电池

图 1 ~ 图 3 为以氢气或乙醇蒸气作燃料在不同温度下以 Ni-ScSZ10、Ni-ScSZ11 和 Ni-ScSZ13 作阳极组成的单电池的 $V \sim I$ 曲线和 $W \sim I$ 曲线. 从图 1 看出,以 Ni-ScSZ10 为阳极的单电池,在 850、800、750 和 700 ℃ 下,其最大的功率密度依次是 521、413、298 和 186 mW/cm^2(氢气)和 486、286、218 和 161 mW/cm^2(乙醇蒸气);而 Ni-ScSZ11 阳极单电池(图 2)与上述温度对应的最大功率密度分别是 586、485、356 和 219 mW/cm^2(氢气)和 541、356、252 和 206 mW/cm^2(乙醇蒸气),对 Ni-ScSZ13 阳极的单电池(图 3),其对应温度的最大功率密度则分别是 710、582、475 和 354 mW/cm^2(氢气)和 669、422、335 和 238 mW/cm^2(乙醇蒸气). 显然,阳极催化层 CeO_2 含量增加,电化学性能也提高. 该阳极催化层可促进乙醇蒸气的重整反应:

$$C_2H_5OH + 3H_2O \longrightarrow 2CO_2 + 6H_2 \qquad (1)$$

图 4 是 Ni-ScSZ13 阳极单电池用乙醇蒸气作燃料在 700 ℃ 下运行 216 h 后 LSCM-CeO_2/Ni-ScSZ 阳极的 SEM 照片. 可以看出,阳极催化层(LSCM-CeO_2)的厚度大约为 8 μm,并且与阳极支撑层 Ni-ScSZ 的界面接触良好.

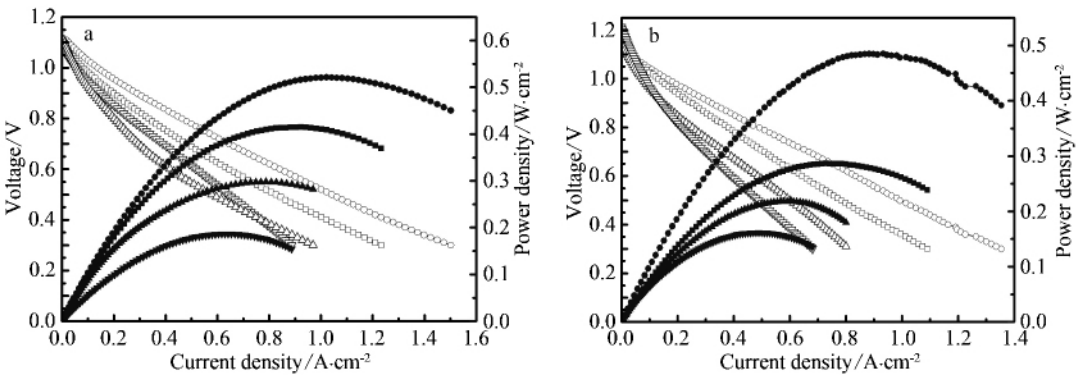

图 1　Ni-ScSZ10 阳极单电池的 $V \sim I$ 曲线和 $W \sim I$ 曲线

工作燃料:氢气(a)、乙醇蒸汽(b),工作温度:(○,●)850 ℃;(□,■) 800 ℃;(▲,△)750 ℃;(▼,▽)700 ℃

Fig. 1　Voltage and power density vs. current density for a SOFC with Ni-ScSZ10 anode while running on humidified hydrogen (a) and ethanol steam (b) at different temperatures: (○,●)850 ℃;(□,■) 800 ℃;(▲,△)750 ℃;(▼,▽)700 ℃

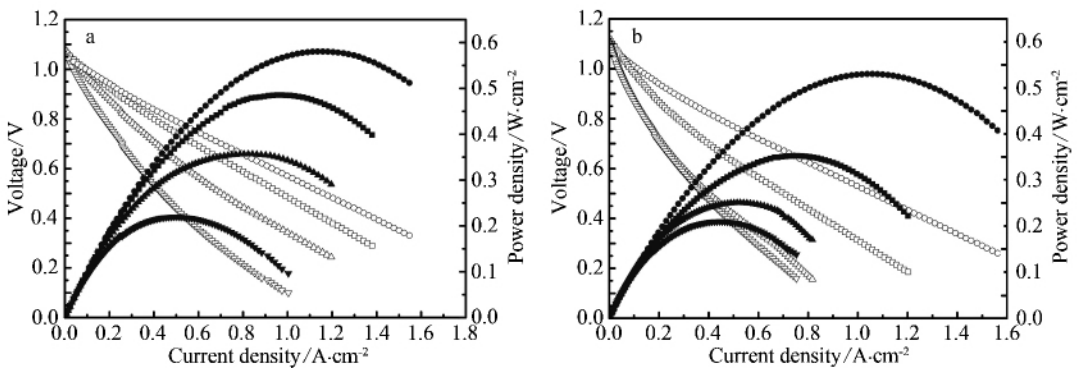

图 2　Ni-ScSZ11 阳极单电池的 $V \sim I$ 曲线和 $W \sim I$ 曲线

工作燃料:氢气(a)、乙醇蒸汽(b),工作温度:(○,●)850 ℃;(□,■) 800 ℃;(▲,△)750 ℃;(▼,▽)700 ℃

Fig. 2　Voltage and power density vs. current density for an SOFC with Ni-ScSZ11 anode while running on humidified hydrogen (a) and ethanol steam (b) at different temperatures: (○,●)850 ℃;(□,■) 800 ℃;(▲,△)750 ℃;(▼,▽) 700 ℃

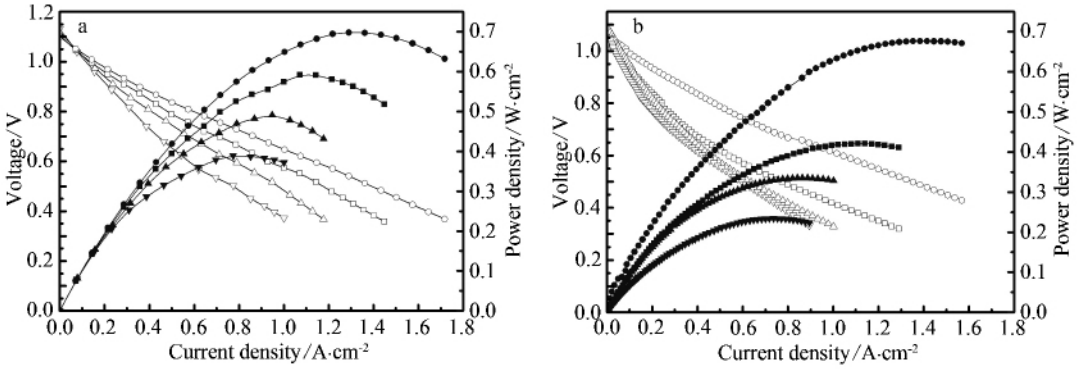

图 3 Ni-ScSZ13 **阳极单电池** $V \sim I$ **曲线和** $W \sim I$ **曲线**
工作燃料:氢气(a)、乙醇蒸汽(b),工作温度:(○,●)850 ℃;(□,■) 800 ℃;(▲,△)750 ℃;(▼,▽)700 ℃

Fig. 3 Voltage and power density vs. current density for an SOFC with Ni-ScSZ13 anode while running on humidified hydrogen (a) and ethanol steam (b) at different temperature: (○,●)850 ℃; (□,■) 800 ℃; (▲,△)750 ℃; (▼,▽) 700 ℃

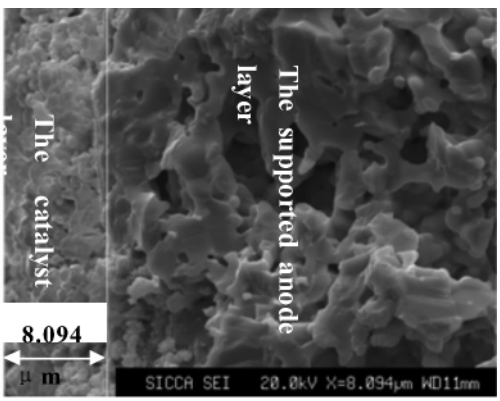

图 4 Ni-ScSZ13 **阳极单电池开路状态 SEM 照片**
燃料:乙醇蒸气,工作温度:700 ℃,运行时间:216 h

Fig. 4 FE-SEM micrograph of the interface LSCM-CeO_2/Ni-ScSZ (Ni-ScSZ13 anode) after fuel cell test in ethanol steam at 700 ℃ for 216 h

2.2 单电池稳定性

图 5 分别显示 Ni-ScSZ10 **和** Ni-ScSZ13 **阳极单电池,以乙醇蒸气为燃料在** 700 ℃ **下不同运行时间交流阻抗图. 由图可见,前者经** 108 h **运行电池性能急剧下降;而后者经** 144 h **运行其性能只略微下降. 说明** CeO_2 **含量增加电池阻抗大减.**

扫描电镜和 X-**射线能量散射分析谱(**EDAX**)分别表明(图略),**Ni-ScSZ10 **阳极单电池其支撑层** Ni-ScSZ **有大量的碳沉积,而** Ni-ScSZ13 **阳极单电池支撑层** Ni-ScSZ **仅存在少量的碳沉积(图** 4**),可见** Ni-ScSZ13 **阳极具有较好的抗碳沉积性能.**

3 结 论

1) **采用双层流延法制备** Ni-ScSZ **阳极支撑层-**ScSZ **电解质复合膜. 在烧结的** Ni-ScSZ **阳极支撑层表面丝网印刷一层** LSCM-CeO_2 **阳极催化层,制备** LSCM-CeO_2/Ni-ScSZ **功能梯度层阳极;**

2) Ni-ScSZ13 **阳极单电池用氢气或乙醇蒸气作燃料于** 850 ℃ **下最大的功率密度分别为** 710 **和** 669 mW/cm^2**,**Ni-ScSZ13 **阳极单电池** 144 h **运行后,性能略下降,表明阳极具有较好的抗碳沉积性能.**

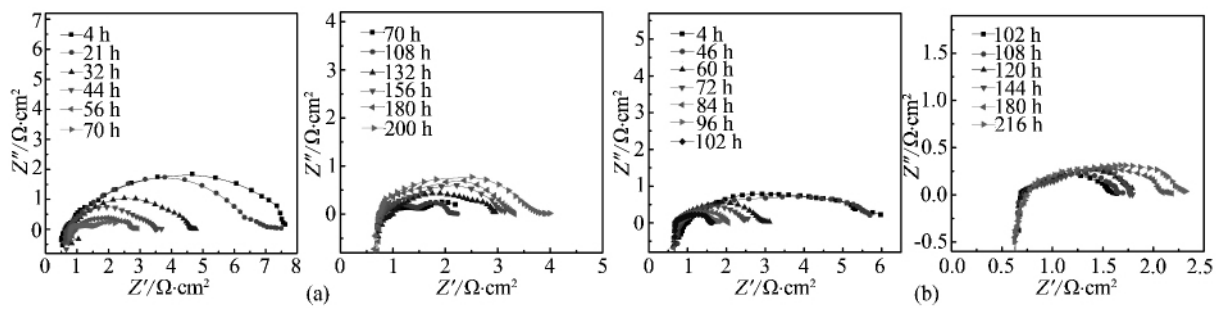

图 5 Ni-ScSZ10(a)**和** Ni-ScSZ13(b)**阳极单电池电化学阻抗谱图 燃料:乙醇蒸气,工作温度:**700 ℃ **开路衰变过程**

Fig. 5 Electrochemical impedance spectra of Ni-ScSZ10 anode (a) and Ni-ScSZ13 anode (b) in ethanol steam at 700 ℃ under open circuit during the aging process

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Fabrication and Characterization of the Ni-ScSZ Composite Anodes with a LSCM-CeO_2 Catalyst Layer in Thin Film SOFC

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Abstract: Solid oxide full cell (SOFC) running directly on hydrocarbon fuels has attracted much attention in recent years. In this paper, a dual-layer structure anode was fabricated by tape casting and screen printing method. The addition of a LSCM-CeO_2 catalyst layer to the supported anode surface yielded better performance in ethanol fuel. The maximum power density reached 710 and 669 mW/cm^2 at 850 ℃ running on hydrogen gas steam and ethanol steam, respectively. No significant degradation in performance has been observed after 216 h of cell testing when the Ni-ScSZ13 anode was exposed to the ethanol steam at 700 ℃. Very little carbon was detected on the anode, suggesting that carbon deposition was limited during cell operation. Consequently, the LSCM-CeO_2 catalyst layer on the supported anode made it possible to have good stability for long-term operation in ethanol fuel due to low carbon deposition.

Key words: electrochemical properties; carbon deposition; catalyst layer; impedance spectroscopy; solid oxide fuel cell