

Short communication

The effect of cerium surface treated ferritic stainless steel current collectors on the performance of solid oxide fuel cells (SOFC)

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Abstract

Laboratory scale solid oxide fuel cells (“button” cells) were operated with untreated or cerium surface treated Fe–22Cr–0.5Mn (composition by weight percent, wt%) ferritic stainless steel current collectors attached to the cathode. After a brief stabilization (or “burn-in”) period, the power density of a cell with the untreated current collector rapidly decreased. By contrast, there was little degradation in power density during testing of cells with the cerium surface treated current collectors. The difference in degradation was attributed to differences in Cr build-up within the cathode. It should be emphasized that the duration of the tests were quite short and longer duration testing is required, however, this initial assessment indicates the treatment may benefit the performance of SOFC with steel interconnects.

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1. Introduction

Chromia (Cr₂O₃) forming ferritic stainless steels are being considered for application as interconnects for planar solid oxide fuel cells (SOFC) [1–5]. The interconnect is a critical component within the SOFC stack, as it separates the anode and cathode and serves to direct the fuel and the air to the respective electrodes. Therefore, it is subjected to both oxidizing and reducing environments, and it is within the electrical circuit of the SOFC. Ferritic steels have physical compatibility (e.g., similar coefficient of thermal expansion) with the oxide components of the SOFC. Electrical conductivity requires that the oxide that forms at the interconnect surfaces be conductive at operating temperatures. Chromia forming alloys meet this requirement; as Cr₂O₃ is a semiconductor at elevated temperatures, whereas Al₂O₃ and SiO₂ are insulators. Hence, there has been considerable effort to develop Cr₂O₃ forming ferritic alloys for interconnects, culminating with Crofer 22APU (ThyssenKrupp VDM) and Hitachi ZMG232 (Hitachi Metals).

Many SOFC designs will operate at temperatures exceeding 700 °C. At these temperatures, ferritic steels lack environmental stability in the SOFC environment, and as a result may degrade the performance of the SOFC through: (i) poisoning of the electrochemical reactions via the evaporation and deposition, or migration, of species such as Cr from the oxide scale on the steel to electrochemically active sites at the cathode–electrolyte interface; (ii) formation of non-conductive oxides, such as SiO₂ or Al₂O₃, at the base metal–oxide scale interface; and/or (iii) excessive oxide scale growth, which may impede electrical conductivity. Consequently, there has been considerable attention on developing coatings to protect steel interconnects in SOFC environments, and on controlling trace elements during alloy production.

It is well known that the addition of a small amount of reactive elements, such as the rare earths elements Ce, La, and Y can significantly improve the high temperature oxidation resistance of both iron- and nickel-base alloys [5–11]. The incorporation of the reactive element can be made in the melt, or through a surface infusion treatment. In fact, both Crofer 22APU and Hitachi ZMG323 contain lanthanum for this purpose, which is added during ingot production. Incorporation of the reactive elements via surface treatment allows for the concentration of the reactive element at the surface where the oxide will form, and thus

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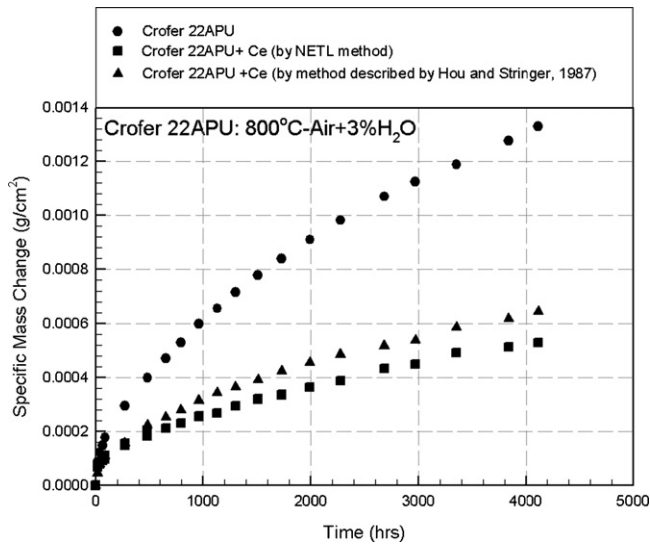


Fig. 1. Influence of Ce surface-treatment on oxidation behavior of Crofer 22APU (after Refs. [12,13]). NETL method described in this paper, and Hou and Stringer method described in Ref. [8]. Notice that both treatments improve oxidation resistance (as measured by weight change) by almost a factor of three times.

may have the most benefit. Recently, we have reported in Refs. [12,13] that cerium surface treatments are effective in improving the oxidation resistance of Crofer 22APU, as illustrated in Fig. 1. The surface treatment retarded scale growth, resulting in thinner oxide scales; and suppressed the formation of deleterious oxide phases, such as the continuous SiO_2 layer that can form at the oxide-metal interface in alloys with high residual Si content (for instance compare Figs. 2–5 found in Ref. [13]). Further, initial area specific resistance (ASR) testing during oxidation revealed that cerium treated coupons had a lower electrical resistance than untreated coupons [12,13]. The present study was undertaken to make a preliminary assessment of the performance of a SOFC that utilizes cerium surface treated ferritic steel as the current collectors.

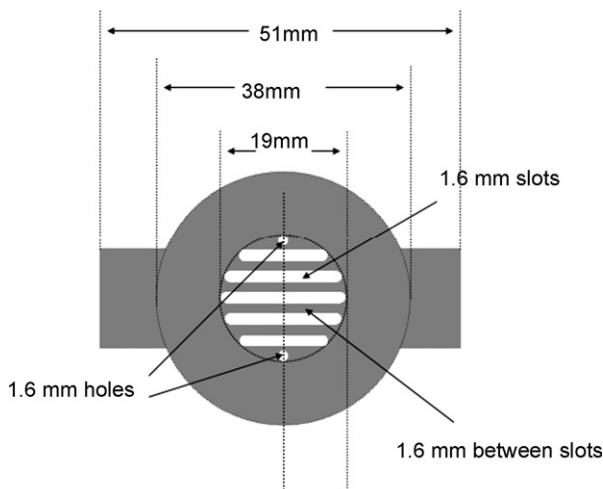


Fig. 2. Schematic of the current collector.

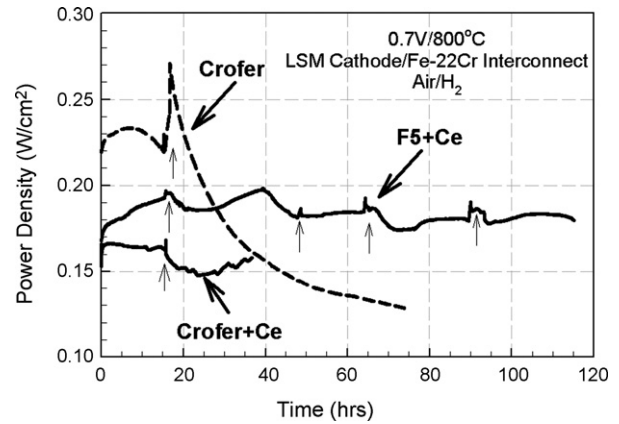


Fig. 3. Power density vs. time for SOFC with untreated Crofer 22APU (Crofer); (2) Ce surface-treated Crofer 22APU (Crofer + Ce); and (3) Ce surface-treated Alloy F5 (F5 + Ce) attached to the cathode. Small arrows indicate when operation was interrupted for periodic voltage sweeps and EIS measurements.

2. Experimental procedure

Two nominally Fe–22Cr–0.5Mn ferritic stainless steels, Crofer 22APU and Alloy F5, were studied (compositional details are listed in Table 1). Crofer 22APU sheet (1 mm thick) was obtained from ThyssenKrupp and Alloy F5 sheet (1 mm thick) was produced in house at the National Energy Technology Laboratory (NETL). The sheets were machined into a current collector with a regular slotted pattern to allow for air flow to the cathode, as illustrated in Fig. 2. Several current collectors were modified with the surface treatment developed at NETL [12,13] for performance comparison with untreated materials. This method consists of painting a polished surface with a slurry mixture containing CeO_2 , a halide activator (sodium chloride) and water. The slurry is dried and subsequently reacted with the alloy during an infusion thermal treatment in a mild vacuum (1×10^{-3} Torr) at 900°C for 12 h. After treatment, excess slurry is removed by

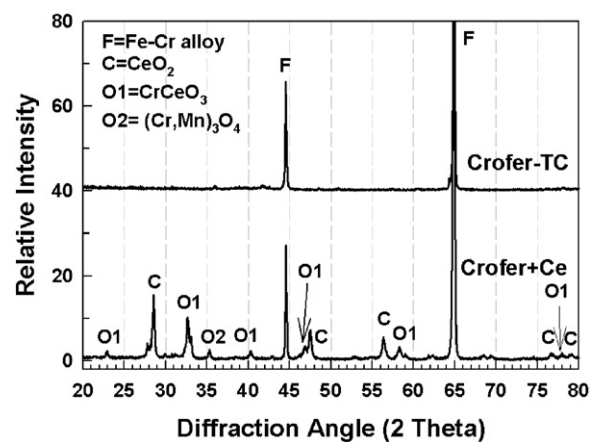


Fig. 4. X-ray diffraction scans of the surface of Crofer 22APU coupons subjected to the Ce surface-treatment (Crofer + Ce) and subjected to only the thermal portion of the treatment (Crofer-TC). This indicates that the pre-oxidation only occurs when the CeO_2 applied to the surface during treatment. (Note the identification of the Cr–Mn oxide is based on the diffraction angle for the 100 intensity peak and the chemical analysis associated with the cross section shown in Fig. 5.)

Table 1
Analyzed chemical composition of alloys (wt%)

Alloy	Fe	Cr	Mn	Ti	Al	Si	O	N	C	S
F5	73.31	22.01	0.44	0.007	0.029	0.022	0.123	0.045	0.008	0.009
Crofer 22APU	75.87	22.75	0.45	0.095	0.11	0.27	0.003	0.012	n/a	n/a

rinsing the treated sample in water and buffing by hand with a scotch-brite® type pad.

Zirconia-based electrolyte supported, 2.5 cm diameter single SOFC (“button cells”) from Nextech Materials were used for this study. These cells consist of 1.27 cm diameter, 50 μm thick $\text{La}_{0.8}\text{Sm}_{0.2}\text{MnO}_3$ (LSM) cathode and 50 μm thick $\text{Ni-Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (Ni-GDC) anode. The cells are also designed with a thin Gd-doped CeO_2 layer at the electrolyte–cathode interface. The ferritic stainless steel current collector and Pt mesh were attached to the cathode and anode, respectively, with Pt paste. Silver current cables and voltage taps were spotted welded onto opposite ends of the steel interconnects and the Pt mesh. It should be emphasized that the surfaces of the untreated interconnects attached to the cathode had a polished finish, whereas the Ce surface-treated interconnects were in the as-treated condition.

The button cell assemblies were mounted between two ceramic flanges and a ceramic o-ring using mica as the sealing material, and were placed inside a split furnace. The cells were first heated to 800 °C for 2 h under a flow of nitrogen on the anode side and air +3% H_2O on the cathode side. When the cells reached 800 °C, a reducing mixture of 10% H_2 and balance N_2 was introduced on the anode side. After 2 h the fuel mixture was changed to a 97% H_2 and 3% H_2O mixture, and the cells

were allowed to equilibrate under these conditions for 2 h prior to testing. The oxidant flow rate was 1000 $\text{cm}^3 \text{min}^{-1}$ and the fuel flow rate was 400 $\text{cm}^3 \text{min}^{-1}$. The cells were operated at a constant voltage level of 0.7 V. The loading on the fuel cell was accomplished using a commercial load box (Agilent N3301A) and a computer recorded the current as a function time. Periodically, the cells were subjected to voltage sweeps from 1.1 to 0 V. Complete details on the button cell testing methodology can be found elsewhere in Refs. [14,15].

3. Results

Results of the button cell tests are presented in Fig. 3 as power density versus time for cells with: (i) untreated Crofer 22APU (Crofer); (ii) Ce surface-treated Crofer 22APU (Crofer + Ce); and (iii) Ce surface-treated Alloy F5 (F5 + Ce) attached to the cathode. Unfortunately, the silver current leads from the cells with the Crofer and F5 + Ce current collectors failed after 78 and 117 h, respectively. That is, the Ag wires physically fractured and were no longer able to conduct current; however, failure did not occur at or near the spot weld. The cell with the Crofer + Ce interconnect was stopped after 38 h of data collection.

As is typical for a SOFC with LSM cathodes and ferritic stainless steel current collectors [16–18], the SOFC with the Crofer 22APU current collector displayed an initial “burn-in,” or “current-treatment,” period during which an increase in power density is observed. This lasted about 10 h, and reoccurred, and was accentuated (the high spike on the curve), after the voltage sweep, which was performed after 16 h of operation. After the “burn-in,” the cell began to rapidly degrade, and at the conclusion of operation the performance of the cell (as measured by power density) decreased by almost a factor of two. Again, this behavior is typical for an SOFC with LSM cathodes and ferritic stainless steel current collectors, and is attributed to Cr poisoning of the LSM cathode [16–22].

The SOFC with the Ce-treated current collectors (F5 + Ce and Crofer + Ce) initially have a lower power density than the SOFC with the untreated current collectors. However, the performance of these cells did not degrade for the duration of the tests, as the power density did not change significantly during testing.

4. Discussion

After surface treatment, CeCrO_3 -type and Cr–Mn oxides formed on the surface of the Fe–22Cr–Mn current collectors, as illustrated by the X-ray diffraction trace shown in Fig. 4 and the cross section shown in Fig. 5. CeCrO_3 -type oxides have been found to form in chromia forming alloys doped with rare earths [23]. The X-ray diffraction results also show that subjecting the

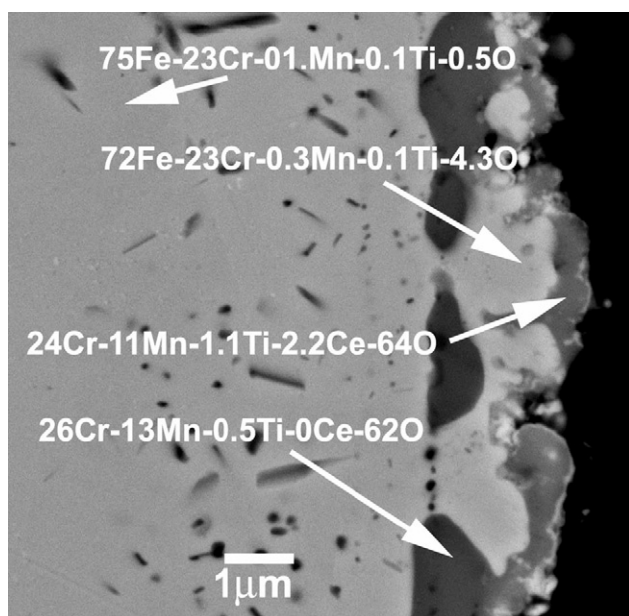


Fig. 5. Cross section of Crofer 22APU after Ce surface-treatment. Compositions for Cr, Mn, Ti, Fe, Ce are in atomic percent and were determined by wavelength dispersive X-ray (WDX) analyses in a field emission scanning electron microscope (SEM).

Table 2
Measured chromium content (wt%) in cathode for button cells operated with Fe–22Cr–0.5Mn current collectors

Microstructure spot (see Fig. 4)	Untreated Crofer 22APU operated for 78 h		Ce-treated Alloy F5 operated for 117 h		Ce-treated Crofer 22APU operated for 38 h	
	Under channel ^a	Adjacent metal ^b	Under channel ^a	Adjacent metal ^b	Under channel ^a	Adjacent metal ^b
(1) Electrolyte	0.00	0.00	0.00	0.00	0.00	0.00
(2) Cathode near electrolyte interface: Ce-rich phase	0.02	0.12	0.02	0.09	0.06	0.00
(3) Cathode near electrolyte interface: La-rich phase	0.48	0.56	0.15	0.24	0.08	0.08
(4) Cathode—middle	0.08	0.09	0.08	0.14	0.11	0.09
(5) Cathode—near current collector	0.09	0.13	0.09	0.17	0.08	0.10

^a Under channel: analysis in a region of the cathode adjacent (or under) the gas channel (slot in current collector).

^b Adjacent metal: analysis in a region of the cathode adjacent (attached) to the metal portion of the current collector.

alloy to only the thermal portion of the treatment, without the presence of CeO₂, does not result in pre-oxidation. As previously reported, coupons subjected to only the thermal portion of the treatment oxidized in an identical manner as polished samples [12,13]. Only in the presence of CeO₂ does pre-oxidation occur during treatment, biasing the surface to form a more slowly growing, and hence, a more protective oxide scale during subsequent exposure.

The differences in initial power density of the SOFCs indicated in Fig. 3 are primarily due to the differences in the initial surface condition of the current collectors. The Crofer current collector was polished, and therefore at the start of the tests, there was no pre-existing oxide layer between the cathode and current collector to resist current flow. By contrast, the cerium treatment produces a thin oxide layer on the metal surface. This oxide layer contributes to the electrical resistance of the SOFC, and the lower initial power density.

A key observation of this study is that the surface treatment appears to minimize Cr migration from the current collector into the cathode. Table 2 lists Cr contents at various locations corresponding to the points indicated on the cross section of the cathode (Fig. 6). The Cr content was determined by wavelength

dispersive X-ray (WDX) analyses in a field emission scanning electron microscope (SEM). Pure Cr was used as the standard for the analyses, with the instrument operating at 15 kV and a beam current of 45 nA. The Cr content was elevated near the cathode–electrolyte interface in all three samples, with the Cr concentrated at the La-rich particles. However, the Cr level was highest in the cathode attached to the Crofer current collector. The Cr content near the interface of this sample was 2–3 times higher than the Cr content near the interface of the sample with the F5 + Ce current collector. This is more significant considering that the sample with the F5 + Ce current collector was operated for a 50% longer time period. However, the Ce-treatment does not completely stop Cr migration from the current collector to the interface, as the Cr level in the cathode attached to the Crofer + Ce current collector, which was operated for only 38 h, is lower than the Cr level in the F5 + Ce sample, which was operated for 117 h, suggesting a slowly increasing Cr content in the cathode with time.

The reduction in degradation due to Cr poisoning can also be attributed to the pre-oxidation that occurs during the Ce-treatment. In fact, the performance characteristics of the SOFC with the Ce surface-treated current collectors were similar to those reported by Simner et al. [16] for an SOFC with a pre-oxidized current collector (see Fig. 13 in Ref. [16]). Simner et al., found that pre-oxidizing a Crofer 22APU current collector at 800 °C for 500 h retarded cell degradation due to Cr poisoning. However, pre-oxidizing the current collector for a shorter duration (100 h at 800 °C) did not minimize Cr poisoning, as the performance of an SOFC with this current collector rapidly degraded in an identical manner to a SOFC with a bare (polished) current collector. In the present study, the initial CrCeO₃-type and Cr–Mn oxides that formed during surface treatment prevented immediate Cr poisoning of the SOFC cell during operation. Time is required for the protective oxides to form at the surface of the untreated current collector; and in the interim Cr can migrate and rapidly poison the cathode. As Simner et al. [16] demonstrated, this time can be significant (>100 h). Clearly, the formation of the initial oxide layer during Ce surface-treatment promotes the formation of protective oxides; and thus, the surface treatment slows Cr migration into the cathode and degradation of the SOFC.

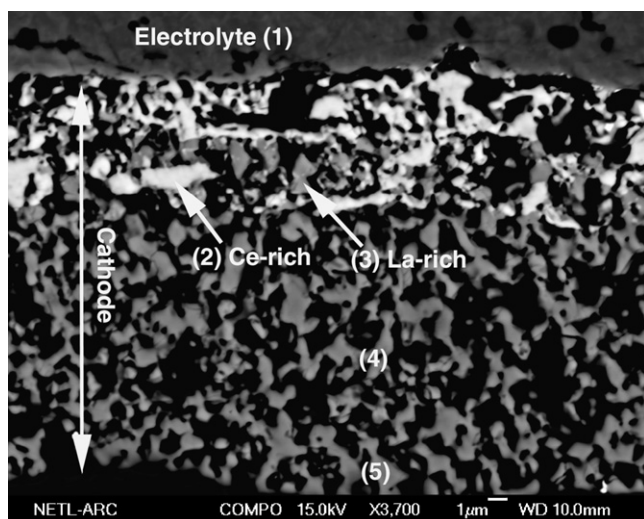


Fig. 6. Cross section of tested cathode. Points identify location of compositional analyses listed in Table 2.

5. Conclusion

The utilization of Ce surface-treated stainless steel current collectors was found to slow the degradation of SOFC with LSM cathodes. Little degradation in power density occurred during testing of SOFCs with Ce-treated stainless steel current collectors attached to the cathode. By contrast, significant degradation in power density occurred with untreated current collectors. The Cr content was lower in cathodes attached to Ce-treated current collectors than in cathodes with untreated current collectors, indicating that the treatment slows Cr migration into the cathode and concomitant poisoning. Longer duration tests are required, and are planned, to determine the effectiveness of the treatment in minimizing Cr poisoning, and to determine if the lower oxidation rate of Ce-treated substrates is also beneficial for SOFC performance.

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