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Impedance spectroscopy of the oxide films formed during high temperature oxidation of a cobalt-plated ferritic alloy

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HIGHLIGHTS

- Co plating was used to synthesize the spinel coating on a ferritic steel.
- Impedance spectroscopy was used to characterize the oxide layers after oxidation.
- Two layers of oxides (Co_3O_4 and Cr_2O_3) were observed for the 2-h sample.
- An additional $CoCr_2O_4$ layer was identified for the 50-, 100-, and 500-h samples.

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ABSTRACT

Impedance spectroscopy was used to evaluate the oxide films formed on cobalt-coated Crofer 22 APU ferritic stainless steel after thermal oxidation at 800 °C in air for different times (i.e. 2, 50, 100 and 500 h). Impedance spectra of the oxide films exhibited two or three semicircles depending on the oxidation time, which correspond to the presence of two or three individual oxide layers. Coupled with scanning electron microscopy/energy-dispersive spectroscopy (SEM/EDS) and X-ray diffraction (XRD), the individual oxide layer corresponding to each semicircle was determined unambiguously. Impedance spectrum analysis of the oxide films formed on the sample after thermal exposure at 800 °C in air for 2 h led to the identification of the low-frequency and high-frequency semicircles as being from Cr_2O_3 and Co_3O_4, respectively. SEM/EDS and XRD analysis of the 500-h sample clearly revealed the presence of three oxide layers, analyzed to be $Co_{3-x}Cr_xO_4$, $CoCr_2O_4$, and Cr_2O_3. Although the SEM images of the 50-h and 100-h samples did not clearly show the $CoCr_2O_4$ layer, impedance plots implied their presence. The oxide scales were assigned to their respective semicircles and the electrical properties of $Co_{3-x}Cr_xO_4$, $CoCr_2O_4$ and Cr_2O_3 were determined from the impedance data.

1. Introduction

Solid oxide fuel cell (SOFC) is a promising electrochemical energy conversion technology for green power generation. The advantages of SOFC include high efficiency, fuel flexibility, environmental friendliness, etc. Nevertheless, this kind of fuel cell has to face an important challenge; the operating temperature is around 800–1000 °C, resulting in the need of components (cathode, anode, electrolyte and interconnect) sustaining severe operating conditions [1]. Ceramic materials used as interconnect are expensive and difficult to machine. Recent developments have lowered the SOFC stack operating temperature to around 600–800 °C, paving the way for the use of stainless steel as interconnect material and thus significantly reducing the stack cost [2,3]. Among various steels, ferritic stainless steels have gained the most attention due to their close match in coefficient of thermal expansion (CTE) with ceramic components used in SOFC [4]. High-temperature oxidation and corrosion process, which occurs for all metallic alloys exposed to SOFC operating conditions, results in oxide scale formation and growth on the alloy surface. The oxide scale can have low electronic conductivity, unmatched CTE with the interconnect steel and cell components, or detrimental reaction with ceramic functional layers. Generally, only chromia (Cr_2O_3) is regarded as prospective oxide scale [5], as it has a relatively high electrical conductivity in comparison to other possible protective scales such as Al_2O_3 and SiO_2 [3,6]. However, Cr_2O_3-forming alloys

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suffer from Cr volatilization. The volatile Cr species could migrate to and poison the cathode, resulting in drastically reduced cathode activity and subsequent degradation of the SOFC performance [7–9]. A significant amount of research efforts has been conducted to address this issue by either the design of new spinel-forming alloys or the development of surface coatings that are electrically-conductive and Cr-blocking.

In spite of the extensive spinel-forming alloy development, the path to low-cost high-performance metallic interconnect is incomplete. Crofer 22 APU, a Cr_2O_3-forming ferritic steel, forms a double-layer surface oxide structure with a $(Cr,Mn)_3O_4$ spinel outer layer atop a Cr_2O_3 inner layer [10]. Cr evaporation from this alloy is significantly reduced by the formation of the thermally-grown spinel surface layer. However, the $(Cr,Mn)_3O_4$ spinel has relatively low conductivity and does not prevent the continuous growth of the subscale Cr_2O_3, which can lead to scale thickening and eventual spallation after long-term exposure. Furthermore, Cr evaporation is not fully mitigated due to the presence of Cr in this spinel. Electrically-conductive and Cr-blocking spinel coatings have also been studied as an alternative approach. Spinel coatings such as Co_3O_4, $(Co,Mn)_3O_4$ and $CoFe_2O_4$ over Crofer 22 APU interconnect have been shown to reduce the growth rate of the native Cr_2O_3 scale, while also acting as a physical barrier to Cr evaporation, thereby improving the long-term performance stability of the SOFC stack [11–13]. The interdiffusion between the Co_3O_4 coating and the oxide scales formed at high temperature on various ferritic steels including Crofer 22 APU have been evaluated along with their scale area specific resistance (ASR) [14–19]. The Co_3O_4 layer has been shown to reduce the overall degradation rate and lower the scale ASR. Larring et al. reported the lowest degradation rate for the Co_3O_4 coating in comparison with various perovskites (e.g. $LaCrO_3$ and $(La,Sr)CoO_3$) and spinels (e.g. Mn_3O_4) [19]. Hansson et al. suggested that the results obtained by Larring et al. could be due to a higher electrical conducting oxide scale rather than a protective scale that reduced the Cr oxidation rate [16].

It is important to understand the interaction of the Co_3O_4 coating with thermally-grown oxide scales, their electrical properties and potential consumption of the Co_3O_4 coating during long-term SOFC operation. Impedance spectroscopy, a non-destructive technique, can be used to assess the presence, growth, and

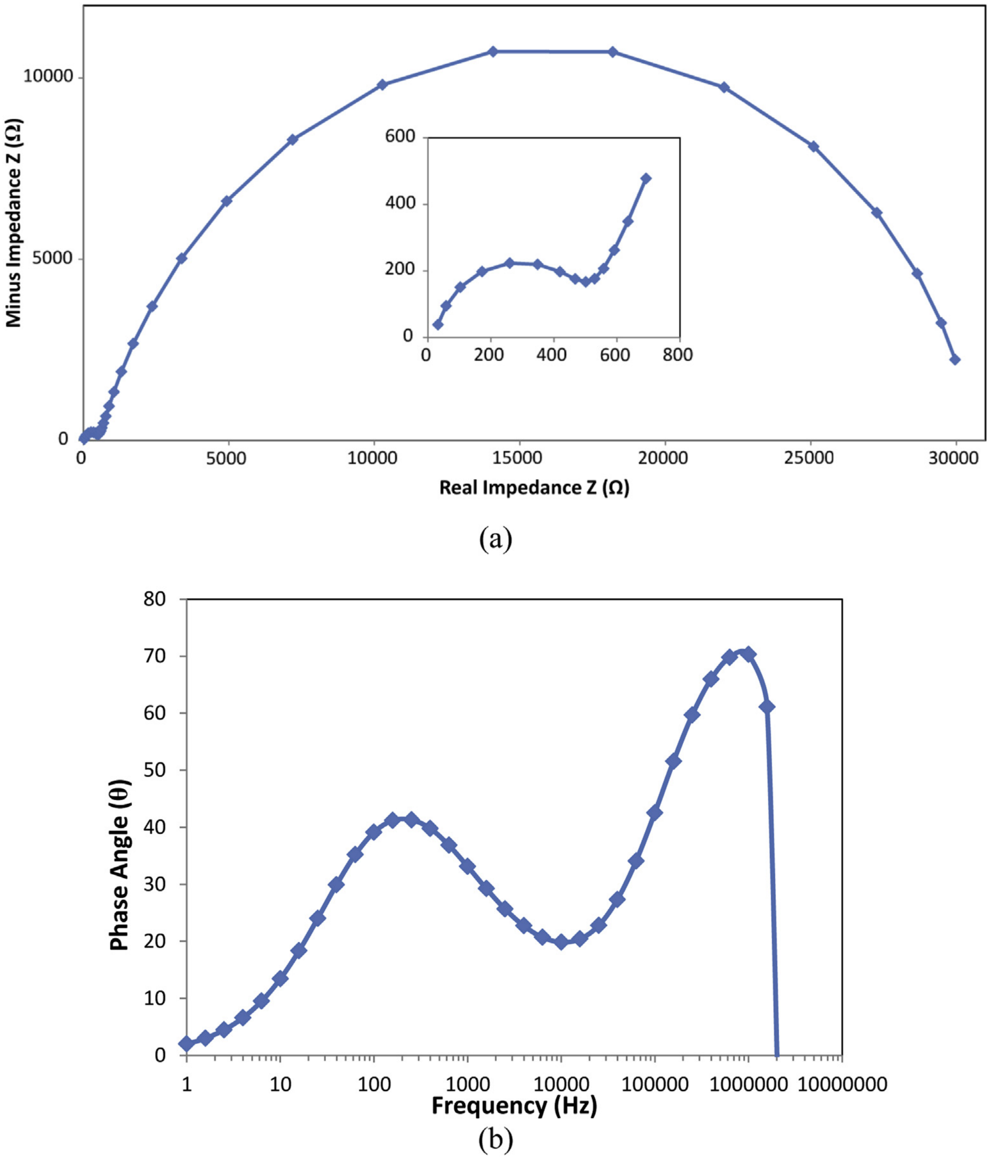

Fig. 1. (a) Nyquist plot with an inset showing the high-frequency-range part and (b) Bode plot for the cobalt-plated sample after oxidation at 800 °C in air for 2 h.