Cation Distribution in Electrically Conductive Spinel Coatings Used as High Temperature Oxidation Protection for UNS430 Stainless Steel

Scott Paulson[1], Ping Wei[2], M. Reza Bateni[2], Anthony Petric[2], and Viola Birss[1]
1 - Dept. of Chemistry, University of Calgary, Calgary, AB T2N 1N4, Canada
2 - Dept. of Materials Science & Engineering, McMaster University, Hamilton, ON L8S 4L7, Canada

Background & Methods: Planar solid oxide fuel cell (SOFC) stack designs (Fig. 1) often employ ferritic stainless steel components due to acceptable compromises in ease of manufacturing, low cost, well-matched thermal expansion properties to the ceramic components, and relatively good electronic and thermal conductivity (1). Unfortunately, the steel interconnect in the cathode chamber, which provides gas manifolding and electronic connection to the cathode, is subjected to flowing, 600 to 850 ^{o}C air. In the process, gas-phase and solid-state reactions between the interconnect and cathode materials lead to "Cr poisoning" of the SOFC cathode (1,2), while excessive long-term oxide scale growth, resulting from pushing the upper work temperature limits of ferritic steels in air, unacceptably increases the contact resistance between the cathode and interconnect (3).

In order to achieve a targeted operational SOFC stack life of 50,000 h, many steel protection solutions have been proposed and tested (4), but cost effective methods for coating complex geometries have been elusive. Recently, a low cost method has been developed for electroplating the steel surface with certain transition metals (Mn, Fe, Co, Cu), combined with thermal annealing in air (5), to generate dense, 30-50 µm thick, mixed-metal spinel oxide films that offer both greatly improved contact resistance (even after 1400 h at 750 ^{o}C in air) (6), and acceptable Cr(VI) volatilization rates (7). What is less clear from this work and other steel coating strategies tested in the literature is whether such coatings can survive continuous exposure to ambient air over 50,000 h (1), where diffusion of Cr cations from the steel into the oxide film may eventual lead to film spalling and direct corrosion of the underlying steel as the critical alloy concentration of Cr falls below the level needed to support a protective, Cr-containing inner oxide layer. In this study, we employ electron microprobe WDX analysis to examine the cation distribution found within the oxide film formed when electroplated Mn and Cu is converted to a spinel oxide film on UNS430 stainless steel as a function of heat treatment time in stagnant room air and flowing dry air (Fig. 2).

Results: Spinel oxide film coated UNS430 stainless steel samples were obtained by electroplating ca 5 µm thick films of Cu and Mn metals, respectively, on acid cleaned UNS430 substrates, followed by heat treatment in ambient air at 750 ^{o}C for a minimum of 1 day. The resulting oxide film is dense and composed of two or more phases, depending on the initial Cu:Mn thickness ratio. The inner oxide layer is dominated by Cr_2O_3, while the outside layers contain spinel phases with varying distributions of Cu, Mn, and Fe.

To determine how this film and the underlying steel evolve over time at 750 ^{o}C/air, three similarly prepared samples were heat treated for 1, 28, and 59 days, respectively. Although the inner Cr_2O_3 layer did not thicken during heat treatment, both the near surface Cr composition of the UNS430 and the metal distribution in the spinel zone changed. For the steel, the Cr depletion zone extended further into the alloy over time, and for the oxide film, the Fe and O content increased, at the expense of Cu and Mn. For spinel-coated UNS430 heated to 700 or 800 ^{o}C under flowing dry air for ca. 100 h, preferential vapor-phase loss of Cu was significant, leading to grain-boundary erosion of the oxide film and generation of new, Mn-rich spinel phases (7). The implications of this work on developing stable oxide coatings for SOFC interconnects will be discussed.

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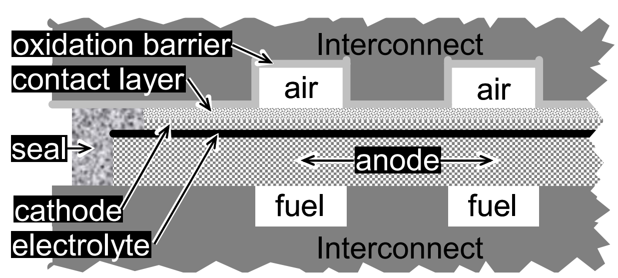

Figure 1. Schematic illustration of a portion of a cell within an SOFC stack.

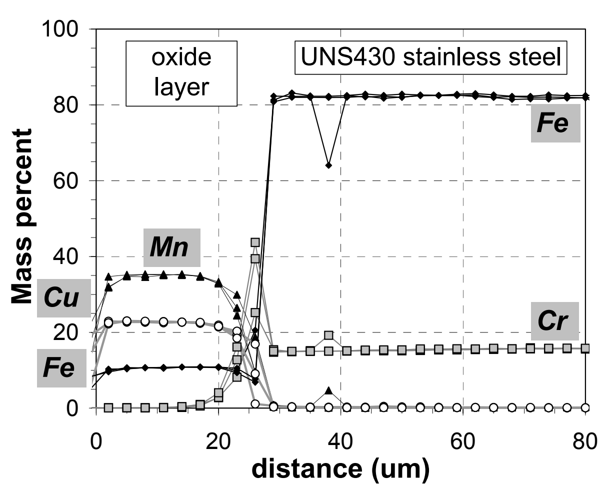

Figure 2. Plot of the results taken from quantitative WDX spot analysis of a polished cross-section of the Cu:Mn coated UNS430 sample (59 days, 750 ^{o}C) taken along three parallel lines extending from the oxide film into the steel.