INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 36 (2011) 4530–4539

Available at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he

Development of chromium barrier coatings for solid oxide fuel cells

Dilip Chatterjee [a,b,*], Samir Biswas [a]

[a] Corning Incorporated, Corning, NY 14831, USA
[b] Director of Research, Oxane Materials Inc, 467 W 38th Street, Houston, TX 77018, USA

ARTICLE INFO

Article history:
Received 22 December 2009
Received in revised form
30 March 2010
Accepted 18 April 2010
Available online 3 June 2010

Keywords:
SOFC
Cathode poisoning
Chromium volatilization
Diffusion coating
Aluminide
Plasma spray
Spinel

ABSTRACT

The performance of electrolyte supported solid oxide fuel cell is impaired primarily due to poisoning of electrodes due to contaminants generated from the metallic components of the stack.

Ferritic stainless steels are commonly used as stack material under severe operating conditions of SOFC environment. However, the high chromium content in this type of steels tends to form gaseous oxides and/or hydroxides which volatilize and condense on various components of stack assembly, particularly cathodes, resulting in performance degradation of the system.

Two types of barrier coatings have been developed to minimize the chromium volatilization. In one case, coatings of oxide species were deposited by processes such as thermal and plasma spraying, and the other is by diffusion coating process such as aluminizing.

This presentation will describe various barrier coatings, barrier properties provided by the coatings, and transpiration measurements adopted to evaluate the efficiency of those coatings.

1. Introduction

In electrolyte supported solid oxide fuel cell (SOFC) stack, a frame capable of withstanding SOFC operating environments is required to support the solid oxide electrolyte sheet of yttria-stabilized zirconia (YSZ). Various types of ferritic stainless steel such as AISI 446, 430 and E-Brite™ (Allegheny Ludlum) were under evaluation as potential candidate frame material (Fig. 1). These steels posses the coefficient of thermal expansion in the range of 11.2–11.6 ppm/°C, which is compatible with that of the 3 mol% YSZ electrolyte, in addition to their stability in both oxidizing and reducing environments at the operating temperature around 750 °C. However, all these steels mentioned above have chromium content in the range of 18–27 wt.%. All types of stainless steels form Cr_2O_3 during oxidation at elevated temperature which acts as a base protective scale. But under fuel cell operating conditions of high humidity and elevated temperature, Cr_2O_3 scale is oxidized to gaseous species such as CrO_3 or $CrO_2(OH)_2$), through the following reactions:

$$2Cr + 1.5O_2\ (g) = Cr_2O_3\ (s)$$

$$Cr_2O_3\ (s) + 1.5O_2\ (g) = 2CrO_3\ (g)$$

$$Cr_2O_3\ (s) + 2H_2O\ (g) + 3/2O_2\ (g) = 2\ CrO_2(OH)_2\ (g)$$

According to Ebbinghaus' calculated and measured thermodynamic data [1], $CrO_2(OH)_2$ (g) is the most dominant

* Corresponding author.
E-mail address: dilip@oxanematerials.com (D. Chatterjee).

0360-3199/$ – see front matter
doi:10.1016/j.ijhydene.2010.04.114

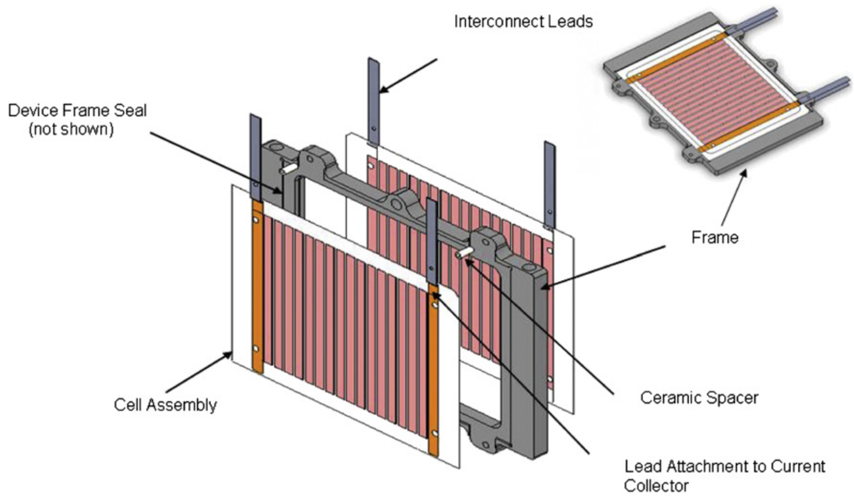

Fig. 1 – A typical electrolyte supported SOFC stack assembly.

volatile component at moderate temperature in the presence of O_2 and H_2O such as in the fuel cell operating environment. However, the above species are reduced at the cathode side causing degradation of the cell performance known as "cathode poisoning" according to the following reactions [2].

$$2CrO_2(OH)_2\ (g) + 6e^- \rightarrow Cr_2O_3\ (s) + 2H_2O\ (g) + 3O^{2-}$$

$$2CrO_3\ (g) + 6e^- \rightarrow Cr_2O_3\ (s) + 3O^{2-}$$

In cathode poisoning, gaseous CrO_3 (g) and $CrO_2\ (OH)_2$ (g) deposit onto the cathode as solid Cr_2O_3 (s) and degrades SOFC performances over time.

Abatement of chromium evaporation from ferritic stainless steels by surface modification of the frame material or by developing a barrier layer is of significant interest in SOFC development.

An effective barrier layer for electrolyte supported SOFC system should possess a few ideal attributes, such as (a) minimum mismatch of thermal expansion coefficients (CTE) between the glass seal materials and the frame materials; (b) electrically non-conductive; and (c) low diffusivity of chromium in it.

This paper summarizes approaches in development of suitable barrier coatings and evaluation of their effectiveness.

2. Approach and details of various coating processes

Considering the advantages and disadvantages of various candidate materials for coating on ferritic stainless steel, it was determined that alumina and/or other mixed oxides (spinel) would meet the criteria of an effective barrier coating on ferritic stainless steels, except for its considerable mismatch of CTE with stainless steels (as noted below in Table 1).

Alumina is dielectric, and dense. It possesses low diffusivity of chromium at high temperature (estimated $\sim 10^{-22}$ m^2/s at 800 °C) [5]). Another important parameter for the barrier coating development is determination of its optimum thickness for suppression of the volatile species migration through the barrier layer.

Theoretical calculations [6] predicted that alumina barrier layer on AISI 446 ferritic stainless steel should be at least in the range of 20 μm thickness to ensure chrome concentration to be well below 5 wt.% at the outer surface of the barrier layer after five years (∼ 40,000 h) of fuel cell operation at 800 °C.

Depending on the methods for application of barrier coating on stainless steel substrate and the desired coating thickness, the coating applications were classified as (a) direct deposition of alumina or other mixed oxides, such as spinel and (b) in-situ formation of thermally grown alumina from diffusion coated substrate as described below.

2.1. *Direct deposition of alumina or other oxides as Cr barrier layer on ferritic stainless steels*

Thermal and Plasma Spray – These are process in which metallic and nonmetallic materials are deposited in a molten or semi-molten state on a prepared substrate imparting properties that the substrate would not otherwise possess. In these methods either an electric or gas source (for thermal spray) or plasma sources (for plasma spray) helps melting alumina powder feedstock. As the molten powder particles impinge with high velocities on to a ferritic stainless steel substrate or on to a SOFC frame, they form a dense coating of

Table 1 – Coefficient of thermal expansion.

Material	CTE at 750 °C (ppm/°C)
Ferritic Stainless Steel–(E-Brite)	11.7[a]
Alumina	8.2[b]

a from reference [3].
b from reference [4].