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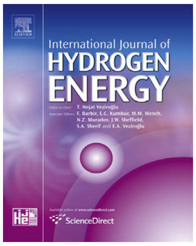

Effect of coatings on long term behaviour of a commercial stainless steel for solid oxide electrolyser cell interconnect application in H_2/H_2O atmosphere

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ARTICLE INFO

Article history:
Received 22 April 2014
Received in revised form
11 July 2014
Accepted 12 July 2014
Available online xxx

Keywords:
High temperature electrolysis
Hydrogen
Interconnects
Ferritic steels
Perovskite and spinel coatings

ABSTRACT

K41X (AISI 441) stainless steel evidenced a high electrical conductivity after 3000 h ageing in H_2/H_2O side when used as interconnect for solid oxide electrolyser cells (SOEC) working at 800 °C. Perovskite ($La_{1-x}Sr_xMnO_{3-\delta}$) and spinel ($Co_3O_4$) oxides coatings were applied on the surface of the ferritic steel for ageing at 800 °C for 3000 h. Both coatings improved the behaviour of the steel and give interesting opportunities to use the K41X steel as interconnect for hydrogen production via high temperature steam electrolysis. Co_3O_4 reduced into Co leading to a very good Area Specific Resistance (ASR) parameter, 0.038 Ω cm^2. Despite a good ASR (0.06 Ω cm^2), $La_{1-x}Sr_xMnO_{3-\delta}$ was less promising because it partially decomposed into MnO and La_2O_3 during ageing in H_2/H_2O atmosphere.

Introduction

Solid oxide electrolyser cells (SOEC) represent a clean way to produce hydrogen. They work as an inverse fuel cell, using air at the anode side and water vapour at the cathode side. According to Zeng et al. [1], hydrogen production via steam hydrolysis may involve less electrical energy consumption than classical low temperature hydrolysis, because of improved thermodynamic and kinetic operating conditions at elevated temperature. But, due to severe corrosive environments (gas and high temperatures), SOEC are faced to material challenges. As for SOFCs technology, a major technical difficulty related to the high temperature steam electrolysis is the development of interconnects efficiently working for a long period (around 25000 h) in high temperature aggressive

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http://dx.doi.org/10.1016/j.ijhydene.2014.07.058

environment. Ferritic stainless steels are among the most promising materials, due to their good high temperature corrosion resistance and their quite good electrical conductivity [2–9]. In this study, a commercial stainless steel containing 18 wt. % of chromium, K41X (AISI 441), was tested as interconnect at 800 °C in $Ar/1\%H_2/9\%H_2O$ atmosphere (cathode side of SOEC) for 3000 h. The electrical conductivity was also evaluated in the same atmosphere. The tests evidenced that uncoated K41X steel is not suitable for SOEC interconnect application in H_2/H_2O atmosphere. The main topic of the paper is to study the effect of coatings on the interconnect behaviour at the cathode side of the SOEC. Surface modification is known to change the behaviour of Ni electrodes for low temperature water electrolysis [10]. But, there is almost no literature about the effect of coatings in SOEC atmospheres for hydrogen production. Based on literature review made for SOFC application, perovksite and spinel oxide coatings appear promising in order to increase the high temperature oxidation behaviour and the electrical conductivity of ferritic stainless steel interconnects [3,11–17]. As a consequence, coatings composed of spinel (Co_3O_4) or perovskite ($La_{1-x}Sr_xMnO_{3-\delta}$) oxide phases were tested. In a previous paper, these coatings showed beneficial effects at the anode side, O_2/H_2O, especially by preventing Cr species volatilization [18]. The present study aims to verify that such coatings could give good performances at the H_2/H_2O side of SOEC as well. The study follows the interconnect degradation for a long period and investigates the role played by $La_{1-x}Sr_xMnO_{3-\delta}$ and Co_3O_4 surface coatings in cathode atmosphere for high temperature electrolysis (HTE).

Materials and methods

Samples preparation

The material selected for this study, K41X (AISI 441), is a commercial stainless steel containing 18 wt. % of chromium (Fe − 18%Cr − 0.58%Si − 0.52%Nb − 0.25%Mn − 0.14%Ti). The as-received samples were cut into squares of 10 mm × 10 mm and 1 mm thick. Note that the samples were not polished before the tests or the coatings.

The perovskite coatings, LSM ($La_{1-x}Sr_xMnO_{3-\delta}$), were prepared by screen-printing process, followed by 5 h annealing at 850 °C in air, in order to improve the compactness of the coating and its adhesion to the substrate. The spinel coatings (Co_3O_4) were applied on the K41X surface by physical vapour deposition (PVD) technique, followed by a crystallization treatment performed during 10 h at 800 °C in air.

Isothermal oxidation tests and oxide scale analyses

In order to study the influence of hydrogen and water vapour on the corrosion behaviour, samples were placed in a horizontal furnace. Isothermal oxidation tests were performed at 800 °C for dwell time up to 3000 h in controlled $10\%H_2/90\%H_2O$ gas mixture. For safety reasons, H_2 was diluted in Ar and the real gas composition used was $Ar/1\%H_2/9\%H_2O$. Gas mixture ($Ar/1\%H_2$) was passed through boiling distilled water. The H_2O fraction was controlled by bubbling gas through a cooling tube ($T = 29$ °C), so that the H_2O partial pressure could be adjusted. The H_2O vol. % was checked using a hygrometer [19].

The weight of each sample was measured before each oxidation test and after cooling at room temperature. Weight difference divided by sample surface area allowed calculating mass gain.

The oxide surface and cross-section morphologies were analysed using a JEOL JSM-7600F scanning electron microscope (SEM) equipped with a field emission gun (FEG). This equipment, coupled with an energy dispersive X-ray (EDX) spectrometer, was used to determine the morphology and the chemical composition of the corrosion products. Phase composition of the oxide scales were characterized by X-ray diffraction (XRD) using Cu Kα ($\lambda = 0.154$ nm) radiation with an incidence angle of 8°.

Oxide scale area specific resistance

All the experimental tests were performed at 800 °C for 3000 h in a flux of controlled $Ar/1\%H_2/9\%H_2O$ gas, representing the SOEC cathode side. Area specific resistance (ASR) measurements were performed in-situ after the 3000 h ageing tests for added 100 h by using a 4-point set up [3]. The voltage value is measured by applying a constant current of 150 mA. According to the Ohm's law ($R = V/I$), the electrical resistance is estimated. ASR parameter is then obtained by multiplying this resistance by the sample surface ($ASR = R \times S$).

Results

Coating characterizations

Fig. 1 shows a SEM observation of the cross-section of Co_3O_4 coated K41X stainless steel. The deposited layer appears homogenous, and porous with a thickness of around 3 μm. EDX analyses indicate that the layer is mainly composed of a spinel oxide Co_3O_4 with some chromia in the internal part. The presence of Co_3O_4 was verified by XRD diffraction patterns. A thin SiO_2 layer is also visible at the metal-oxide interface. Note that the Ni layer at the top surface of the spinel oxide coating was deposited in order to protect the sample and the oxide scales during the cross-section preparation.

The LSM coating appears homogenous and porous with a thickness of around 20 μm (Fig. 2). EDX analyses revealed the presence of La, Sr, Mn and O in the external part of the coating. Cr and O are identified in the inner part very close to the underlying substrate (see arrow in Fig. 2). XRD diffraction patterns evidence the presence of several phases: a phase rich in La identified as $La_{0.9}Sr_{0.1}MnO_3$, a spinel oxide $La_{1.2}Sr_{0.8}MnO_4$ and a manganese oxide MnO. A very thin SiO_2 layer is also observed at the metal-coating interface.

Oxidation and electrical behaviours

After 3000 h ageing in $Ar-1\%H_2-9\%H_2O$ at 800 °C, the oxide scale formed on the uncoated K41X is homogenous. Small grains with irregular shapes are covering the surface (Fig. 3a). EDX analyses show the presence of Cr, Fe and Mn. XRD

Please cite this article in press as: Ardigo MR, et al., Effect of coatings on long term behaviour of a commercial stainless steel for solid oxide electrolyser cell interconnect application in H_2/H_2O atmosphere, International Journal of Hydrogen Energy (2014), http://dx.doi.org/10.1016/j.ijhydene.2014.07.058