Investigation of the Cr volatilisation using the ceramic phase collector technique

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Abstract. An effect of chromium contamination in the lanthanum strontium manganite (LSM) cathode which is a component of solid oxide fuel cell (SOFC) leads to degradation of the device. This is caused by volatilisation of Cr-species from the iron-chromium alloy at high temperature. In this work, the ceramic phase collector technique was used to evaluate the Cr volatilisation. To prove the effectiveness of this method, AISI 430 ferritic stainless steel samples with and without cobalt (Co) spinel coatings were used to compare the Cr condensation in the LSM ceramic. The coatings were produced by electroplating followed by a heat-treatment process. The samples were characterised using SEM with EDX and XRD to confirm the microstructure and the formation of Co spinel. It was found that chromium migration was restrained for coated samples, in contrast the Cr-species deposited in the LSM for uncoated samples. The chromium volatilisation evaluated by the contents of Cr species in the LSM collector was compared to the traditional condensation technique which analysed chemical contents by inductively coupled plasma-mass spectrometry (ICP-MS).

1. Introduction

Recent decades, striving for new sources of sustainable energy has been urgent need to overcome the global energy crisis and environmental problems. Many researches are focused on the chemical reaction to generate electricity directly, such as a battery or a fuel cell due to its efficiency in energy transformation compared to the traditional combustion heat engine. Among many types of fuel cells, the solid oxide fuel cell (SOFC) is an important key device expected to be the next generation of sustainable energy source. An SOFC operates at the intermediate high-temperature range of 600–1000 °C and yields electrical energy by means of oxygen reduction to oxygen ion and ion migration from the cathode to the anode through the ceramic electrolyte. In case of utilising hydrogen as a fuel gas, at the anode side pure water is the product of the oxidation reaction from the fuel cell, thus the SOFC is also known as the clean energy generation device which benefits for low greenhouse gas emission [1, 2].
Interconnect is a component used for connection between SOFC stacks and conveying electricity. The ferritic stainless steel (FSS), which is an iron-chromium (Fe-Cr) alloy, has a potential to be applied as the interconnect due to its operation cost, machinability and mechanical properties. The FSS is not only suitable in the physical term such as compatible thermal expansion with cathode ceramic but also stability in chemical properties both in reducing and oxidising atmosphere [3]. At the operating temperature of SOFC, the passive chromium oxide (Cr₂O₃) is generally formed on the surface of the stainless steel. However, the problem occurs when SOFC stacks are operated for a long period of time, the containing Cr is oxidised and becomes vapour phased Cr-species, CrO₂(OH)₂ or CrO(OH)₂ [4]. The condensation of vaporised Cr-species is burdened at the cathode which is an ionic conductor. Having been attached by Cr-species makes them lose their functionalities; hence the operation of SOFC fails [3, 5-7]. To prevent this phenomenon, coating the spinel conductive ceramic on the interconnect FSS has been reported on hindering the migration of Cr and reducing the volatilisation of Cr-species [8, 9].

With regard to vapourisation study of Cr-species, many methods for evaluation the amount of volatilised Cr have been developed. A well-known method is the condensation method which can detect the small amount of Cr in the level of 1 ppb using with the inductively coupled plasma-mass spectrometry (ICP-MS) [10]. However, this method needs multiple steps and careful efforts to restore condensates in the column [11]. Another example is the ceramic phase collector technique. This technique is relatively simple compared to the former method. It is performed by enclosing the test material within ceramic plates. Han and co-workers [12] quantitatively reported Cr volatilisation of Crofer22APU using silicon wafer collectors, however, this method needs to analysed by Rutherford backscattering spectroscopy (RBS) which is difficult to access for most researchers.

Therefore, in this work lanthanum strontium manganite (LSM), the cathode material used in SOFCs, has been proposed to be a ceramic collector for evaluation Cr volatilisation. The quantity of Cr was analysed using SEM with EDX. The FSS grade AISI430 samples with and without Mn spinel coating were applied to evaluate the Cr volatilisation in comparison with those evaluated by the traditional condensation method.

2. Experimental

2.1. Sample preparation
The AISI 430 stainless steel was selected for this study. The chemical composition (wt.%) measured using an emission spectroscopy (SPECTRO Model SPECTROMAXx) is shown in Table 1. The samples were provided as the square shape of 25 × 25 mm² coupons with the thickness of 1 mm. All surfaces of samples were polished until 800 grade abrasive paper and cleaned by alcohol in an ultrasonic cleaning machine for 5 min then dried in blow air. For the electroplating process, the electrolyte solution was described in detail in the previous article [13]. The electroplating condition was carried out by using a direct circuit (DC) with current density of 200 mA cm⁻² for 20 min and cleaned with deionized water (DI). After the electroplating process, the coated samples were subjected to heat treatment in oxygen atmosphere for 24 h at 600 °C which is named the pre-oxidation step. The surface morphologies of heat-treated samples were characterised by a standard scanning electron microscope (SEM) with an energy dispersive X-ray spectroscopy (EDX). The phase structures were identified by a standard XRD diffractometer with Cu Kα radiation.
| Table 1. Chemical composition of the AISI 430 stainless steel in weight percent. |
|-----------------|---------|---------|---------|-------|-------|---------|
| Cr      | Mn    | Si     | Ni     | C     | P     | Fe                |
| 16.92   | 0.326 | 0.295  | 0.155  | 0.042 | 0.018 | Balance           |

2.2. Ceramic phase collector
The yttria-stabilized zirconia (YSZ) powder of 100 g was mixed with the ethanol solution 60 cm$^3$ and polyvinyl butyral (PVB) 1 g which as the electrolyte support. The mixed solution was ball milled for 6 h. The size of powder was selected with the sieve mesh at 75 µm. The pellet of powder was prepared from 2 gram of weight and pressed into a coin shape with a diameter of 20 mm and thickness of 2 mm. The YSZ pellets were sintered in air at 1400 °C for 2 h with 5 °C min$^{-1}$ of a heating rate. The lanthanum strontium manganite (LSM) was used as the cathode. LSM powder was mixed with the glycerol at a weight ratio of 2:1 to obtain a cathode solid solution. The solution was brushed onto one-side of each YSZ pellet. The thickness of cathode was 3 µm controlled by adhesive tape. The cathodes with electrolyte support were subsequently calcined at 1200 °C for 2 h to obtain the ceramic phase collector.

2.3. Oxidation
The isothermal treatment was performed in a horizontal tube furnace with a gas flow which was 20 vol.% water vapour oxygen (O$_2$-20%H$_2$O) for 210 h. In order to generate the water vapour, the oxygen gas with a flow rate 100 ml min$^{-1}$ was delivered downward to the humidity generator with the temperature of water set at 59.4 °C. The sample was placed in the heating zone of the horizontal tube. The furnace was heated from room temperature to 800 °C with a heating rate of 0.5 °C s$^{-1}$. The oxidation was examined under the isothermal temperature at 800 °C for 210 h in O$_2$-20%H$_2$O.

3. Result and discussion

3.1. Formation
Figure 1 shows the XRD result of the spinel coated AISI 430 FSS sample after pre-oxidation in oxygen at 600 °C for 24 h. Two types of cobalt oxide are identified the cubic structure with the peak position matched with the database of Co$_3$O$_4$ (ICDD 09-0418) and CoO (ICDD 43-1004). A small amount of CuO matched with the database of CuO (ICDD 41-0254) is observed on the surface. The Cu element is a nobler metal in solution when it is compared with Co and Mn elements. The standard electrode potential of Mn/Mn$^{2+}$, Co/Co$^{2+}$ and Cu/Cu$^{2+}$ are $-1.185$, $-0.28$, and $0.3419$ V vs. standard hydrogen electrode (SHE) [14], respectively. This indicate that the Cu ion in solution easily deposition on the surface. The database of Fe (ICDD 87-0722) is showing the existence of the bcc Fe or FSS.
Figure 1. XRD pattern of the spinel coated AISI 430 ferritic stainless steel sample after pre-oxidation in oxygen at 600 °C for 24 h.

3.2. Microstructure analysis

Figure 2 shows the cross-section SEM images using the backscatter electron (BSE) mode of the bare AISI 430 ferritic stainless steel and the spinel coated AISI 430 ferritic stainless steel samples. The images show that the uniform thermal oxide scale has grown on the surface with thickness of 3.3 µm in average and the standard deviation of 1.8 µm for the bare sample. The result of the EDX line scan shows the distribution of Fe, Cr and O across the sample. However, these results are difficult to distinguish between the thermal oxide scale and the steel substrate. Nevertheless, many researchers reported that the Cr$_2$O$_3$ and Mn-Cr spinel oxide were generally observed on the stainless steel when they were oxidised in a humidified atmosphere at high temperatures [11, 15-22]. The formation of the thermal oxide scale should be Cr$_2$O$_3$. On the other hand, for the spinel coated sample, as shown in figure 2 (b), the average thickness thermal oxide scales is 14.5 ± 6.6 µm. The cross-section SEM image using backscatter electron (BSE) mode and the EDX line scan across interface between the spinel coating and the thermal oxide scale and interface between the thermal oxide scale and substrate. The results obtained from the EDX line scan show that the two different layers can be distinguished in the thermal oxide scale for the spinel coated sample. The relatively high intensity of Fe, Co and O were observed at the interface between the spinel coating and the thermal oxide scale. These results agreed the previous work done by Wu et al. [23] who reported that the top layer of a scale layer is formed by (Mn, Co, Fe)$_3$O$_4$ spinel for the cobalt-coated and Mn-Co coated samples. For the inner layer of the thermal oxide, the Mn, Cr and O were detected. It indicated that formation of the thermal oxide scale was corresponding to the Mn-Cr spinel oxide. The thermal oxide scale containing the Mn, Cr and O at inner layer should be MnCr$_2$O$_4$. The assumption was confirmed by Yang et al. [8, 24]. They reported that the coated spinel sample showed the presence of Cr$_2$O$_3$ and MnCr$_2$O$_4$ on the oxidised sample after oxidation in air at 800 °C up to 100 h, with regard to the results of XRD and SEM.
Distance (µm)

Intensity (a.u.)

Fe
Cr
O

Distance (µm)

Intensity (a.u.)

Fe
Cr
Co
Mn
Cu
O

(a)

(b)

Figure 2. SEM-BSE image and EDX line scan across interface of sample (a) between the thermal oxide scale and AISI 430 stainless steel and (b) between the spinel coating and AISI 430 stainless steel after oxidation in oxygen with 20% water at 800 °C for 210 h.

3.3. Ceramic phase collector

The SEM images obtained from the fractured sample without epoxy mounting were taken using the secondary electron mode at the interface between electrolyte layers and the LSM cathode collectors as shown in figure 3. The average thickness of LSM cathode is 16.6 µm with 1.6 µm in the standard deviation. In order to measure the Cr-species volatilisation rate, the Cr composition is considered at only the interface between electrolyte layer and the LSM cathode collector. For the AISI 430 ferritic stainless steel, the formation of the thermal oxide scale is Cr$_2$O$_3$ as mentioned in figure 2 (a). The vaporisation of Cr$_2$O$_3$ can generate the gaseous of Cr-species as CrO$_2$(OH)$_2$ according to Reaction (1) [11, 25, 26].

$$\text{Cr}_2\text{O}_3(s) + \frac{3}{2}\text{O}_2(g) + 2\text{H}_2\text{O}(g) \rightarrow 2\text{CrO}_2(\text{OH})_2(g)$$

(1)
Volatilised Cr can diffuse through the porous cathode ceramic and accept electron as an oxidising agent. The electrochemical reduction of \( \text{CrO}_2(\text{OH})_2 \) will react at three phase boundaries (TPB) site lead to the deposition of \( \text{Cr}_2\text{O}_3 \) product as explained in Reaction (2) \[27, 28\].

\[
2\text{CrO}_2(\text{OH})_{2(g)} + 6e^- \rightarrow \text{Cr}_2\text{O}_3(s) + 2\text{H}_2\text{O}_{(g)} + 3\text{O}^{2-}
\]

\( \text{(2)} \)

![Figure 3](image)

**Figure 3.** The SEM images at the interface between electrolyte layers and the LSM cathode collectors after being affixed with (a) bare AISI 430 stainless steel and (b) the spinel coated AISI 430 ferritic stainless steel after oxidation in oxygen with 20% water at 800 °C for 210 h.

The element concentrations at the interface between electrolyte layers and LSM cathode collectors were shown in table 2. For the AISI 430 ferritic stainless steel, the presence of Cr (1.61 wt.%Cr) is detected at the interface between the electrolyte layer and the LSM cathode collector in figure 3 (a). The result has shown that the accumulation of chromium is mainly detected from the cathode surface to the electrolyte/cathode interface. For the spinel coated sample, the EDX cannot detect the amount of chromium deposition at the electrolyte/cathode interface as shown in figure 3 (b). The results are believed that the spinel coated sample has sufficient efficiency in inhibition outward chromium diffusion.
Table 2. Element composition (wt.%) by using EDX point analysis at the interface between electrolyte layers and LSM cathode collectors after oxidation in oxygen with 20% water at 800 °C for 210 h.

| Sample                        | Weight percent (wt.%) |
|-------------------------------|-----------------------|
|                               | La  | Zr  | Mn  | Cr  | O   |
| AISI 430 stainless steel      | 35.54 | 24.97 | 15.79 | 1.61 | 21.79 |
| Spinel coated AISI 430 stainless steel | 42.61 | 24.28 | 17.73 | -   | 15.38 |

3.4. Microstructure analysis
The chromium deposition at electrolyte/cathode interface was measured from semi-qualitative of EDS analysis. Two assumptions about the Cr deposition were done as follows. Firstly, the Cr accumulation was not only present at the TPB site but also could be observed at the electrolyte/cathode interface [27]. Secondly, the volatilised Cr-species was critically considered to be unable to diffuse through the denser electrolyte support. Thus, it was assumed that the transport of Cr from the substrate was restricted at the electrolyte/cathode interface zone. The equation can be expressed as following:

\[
Cr\text{ collected rate } = \frac{wt\%CrL_{\text{cat}}}{\rho_{\text{cat}}t} \times 100
\]

Here \( \rho_{\text{cat}} \approx \rho_{\text{LSM}} \) is the LSM density of 6.5 g cm\(^{-3}\) [29, 30]. \( L_{\text{cat}} \) is the cathode thickness in cm and \( t \) is the exposed oxidation time in s. The wt.%Cr is weight percent of chromium which is obtained from EDX results.

Figure 4 showed the chromium volatilisation rate for stainless steel measured by different methods. The circle symbols are the rates of chromium volatilisation measured by a condensation method. The square symbols are the rates as measured by the ceramic phase collector method. The white and grey colours refer to the oxidised atmosphere in air and oxygen, respectively. The two results of the chromium volatilisation rates were obtained by the ceramic phase collector. Jin and Lu [31] studied the tri-layer sample YSZ/LSM/AISI 441 with different LSM stoichiometry. They investigated the Cr-species distribution by XPS elemental analysis. Among the porous LSM layer with 30 um thickness, the LSM 105 showed the lowest Cr concentration of 2.4 at.% and 11.5, 17.1, 69.0 at% of Sr, Mn and La, respectively, at the YSZ/LSM interface after heat treatment in air at 800 °C for 500 h. The other three results were obtained using a condensation method with ICP-MS. For humid air with 10% water, Young and Pint [32] compared the different of the calculated and measured Cr loss by evaporation from Fe-20Cr-25Ni-Nb at 800 °C up to 5000 h. They reported that the rate of Cr loss which was predicted by mass transfer calculation. The measured Cr loss rate was 31% lower than that of the calculation. Gannon et al. [33] reported the Cr transport rate was approximately similar to the result of Kurokawa et al. [34]. The AISI 430 stainless steels were exposed in humid air at 800 °C with the Cr transport rate of \( 1.0-1.1 \times 10^{-10} \) g cm\(^{-2}\) s\(^{-1}\). In the figure, it can be seen that, the chromium volatilisation rates obtained by ICP-MS are near the tendency line (the dash line) of those measured by the ceramic phase collector method. This means that the ceramic phase collector method can be used to evaluate the chromium volatilisation.
Figure 4. Chromium volatilisation rate with the different chromium collector method as a function of % water vapour compared with literature [31-34].

4. Conclusions
AISI 430 FSS samples with and with coated spinel coatings were investigated to measure the Cr-species volatilisation. The isothermal heat treatment was performed at 800 °C for 210 h in O₂-5%H₂O. In order to estimate the amount of chromium, the ceramic phase collector method was utilised and compared with the traditional condensation method with ICP-MS.

1. The formation of spinel oxide was detected at after pre-oxidation in oxygen at 600 °C for 24 h. The spinel coated AISI 430 FSS was identified to the cubic structure of Co₃O₄ and CoO and a small amount of CuO. After the isothermal oxidation process, the formation of thermally grown oxide was observed on the surface of the uncoated sample and spinel/substrate interface of the spinel coated sample.

2. The vaporisation of chromium from the spinel coated AISI 430 FSS was inhibited by the spinel coating. At electrolyte/cathode interface was unable to detect the amount of chromium deposition. Meanwhile 1.61 wt.% of chromium concentration was detected for the uncoated AISI 430 sample.

3. The estimation of chromium volatilisation was done using the ceramic phase collector method. The Cr measurement was simplified by the conversion the semi-qualitative of the EDS result to the quantitative data. For the ferritic stainless steel, the chromium volatilisation rates were in the same order of 10⁻¹⁰ g cm⁻² s⁻¹ compared with the traditional condensation methods.

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