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The Effect of Pre-heat Treatment of AluChrom 318 on the Corrosion Behaviour and Cr Evaporation in SOFC Cathode Air Pre-heater

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An extremely low Cr evaporation rate was confirmed for the alumina-forming alloy (AluChrom 318) used in an SOFC Cathode Air Pre-Heater application in our previous work. In the current study, a pre-heat treatment was applied on the AluChrom 318 in order to achieve the formation of a protective alumina scale prior to SOFC application, further decreasing the oxidation rate and Cr evaporation. To examine this further, the effect of pre-heat treatment on the AluChrom 318 was investigated with two variables, namely; temperature (800 to 1100 °C) and dwelling time (0.5 to 4 hours). The results in this study show that the AluChrom 318 pre-treated at 1100 °C for 1 hour will form an α -Al₂O₃ scale leading to a 98% reduction of oxidation rate and 90% reduction of Cr evaporation compared to the non-treated AluChrom 318 under simulated SOFC cathode conditions.

Introduction

A heat exchanger is used in a solid oxide fuel cell (SOFC) system in order to bring the temperature of the air entering the cathode to temperatures close to that of the SOFC stack. Cathode air preheaters (CAPHs) are usually made of stainless steel; however, at SOFC cathode conditions (3% humidified air), typical stainless steel used in commercial heat exchangers allows Cr to evaporate, causing SOFC cathode poisoning and degradation, and therefore reducing the SOFC performance and lifetime. Our previous work has proven that the alumina-forming alloy (AluChrom 318) forms an alumina layer on its surface which acts as a protective scale and reduces the Cr evaporation rate to an order of magnitude lower than chromia-forming alloys (1). However, longer-term industrial operation of the AluChrom 318 heat exchanger plates under SOFC cathode environment showed a large amount of Cr₂O₃ formation around the exhaust outlet (cold zone) and a fast Al oxidation rate around the exhaust inlet (hot zone). This was due to a lower-than-optimal temperature in the cold zone that delayed the formation of the protective scale. For material optimisation, a pre-heat treatment was therefore applied to allow sufficient formation of an alumina scale on the AluChrom 318 prior to the application in SOFC environments. Studies on the effects of pre-treatment on alumina-forming alloys have been reported in the literature (2,3), showing corrosion resistance to be hugely improved. However, the previous pre-treatments were mostly performed at extremely high temperature (1200 °C) with long dwelling time (12 hours) which will considerably increase the cost of production if integrated into CAPH manufacturing. Thus, in the current work, the pre-treatment of the AluChrom 318 was performed directly in air atmosphere with relatively low temperatures (800 to 1100 °C) and short dwelling time (0.5 to 4 hours), which makes the pre-treatment process cost-effective and suitable

for industrialisation. The aim of the present work was to study the effect of pre-treatment temperature and time on the phase formation of alumina scale and measure the chromium release from the AluChrom 318 pre-treated at different conditions by means of a denuder technique (1). The suitability of pre-treatment for AluChrom 318 for SOFC CAPH application concerning the Cr retention capability will be discussed.

Experimental Method

Materials

0.3 mm thick sheet of AluChrom 318 with the composition shown in Table I was used for this study. The sheet was cut into coupons of $15 \times 15 \text{ mm}^2$. The as-received samples were cleaned in acetone and ethanol for 10 min each using an ultrasonic bath before conducting any experimental tests.

Table I. The composition of AluChrom 318 employed in this research in wt.%.

(wt.%)	Fe	Cr	Mn	Al	Ni	Si	Nb	W	Others
AluChrom 318	Bal.	18.8	0.21	3.58	0.24	0.32	0.73	2.02	Hf: 0.06; Y: 0.07; Zr: 0.03 Cu: 0.03; C: 0.01; N: 0.01

Pre-heat Treatment

The effect of pre-heat treatment on the AluChrom 318 was investigated with regards to two variables: temperature and dwelling time. All the pre-heat treatments were conducted in a tubular furnace (Vecstar HZ ST 1100) with the samples standing vertically on an alumina plate in air atmosphere (no flow). The samples were heated to the target temperature with a heating rate of $10 \text{ }^\circ\text{C}/\text{min}$, and held at the target temperature for the programmed duration, and subsequently, cooled down to room temperature inside the furnace. The matrix of pre-treatment conditions is shown in Table II.

Table II. The matrix for pre-heat treatment conditions of AluChrom 318.

Temperature	Dwelling time		
800 °C	1 h	2 h	4 h
900 °C	1 h	2 h	4 h
1000 °C	1 h	2 h	4 h
1100 °C	30 min	1 h	2 h

Exposure Test

For the Cr evaporation test, the volatile Cr species were measured by isothermally exposing three identical samples for 168 hours continuously using a denuder technique in a tubular furnace at $850 \text{ }^\circ\text{C}$ in $6.0 \text{ L}/\text{min}$ air flow with 3% water content. Details on the denuder technique can be found in Ref (1,4). Inductively coupled plasma-optical emission spectrometry (ICP-OES) was applied on the obtained Cr-containing solution to quantify the total amount of Cr species evaporated. A high temperature oxidation test was additionally carried out by exposing various pre-treated samples simultaneously in one furnace at the same temperature and gas flow for a total time of 500 hours. However, the samples in the oxidation test were removed after cooling the furnace at increasing time intervals for gravimetric measurement and characterisation.

Characterisation

Gravimetric measurements were recorded as a function of time after each isothermal exposure test by evaluating the mass change from three coupons exposed simultaneously using a Cubis Micro Balance (MSA2.7S0TRDM). The surface microstructure of non-treated and treated samples was studied by scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDX) (Tabletop Microscope TM3030, Hitachi-Hitec) before and after the exposure tests. The crystalline structure of the oxides formed on the samples after pre-treatment was analysed by X-ray diffraction (XRD) (D2 PHASER 2nd generation, Bruker) with a Co-K α radiation ($\lambda=0.179026$).

Results and Discussion

Pre-heat Treatment

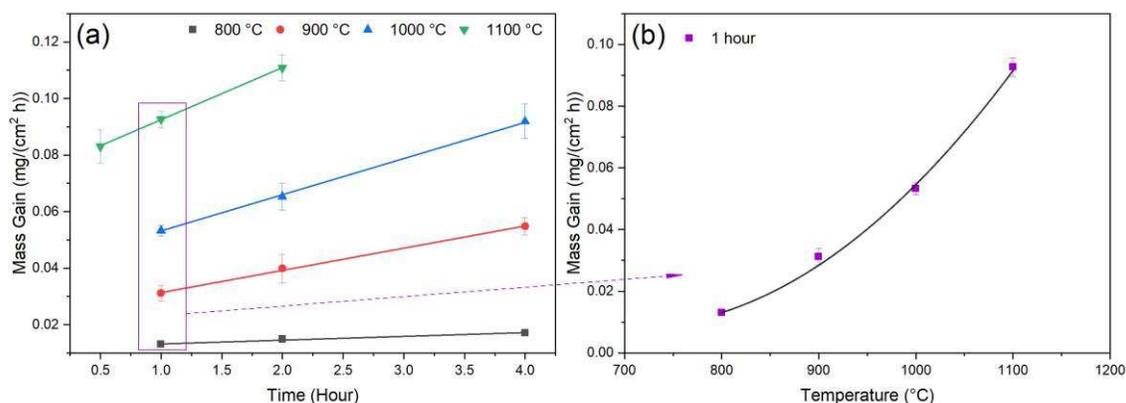


Figure 1. (a) Mass gain of the AluChrom 318 pre-treated at 800 °C for 1, 2 and 4 hours, 900 °C for 1, 2 and 4 hours, 1000 °C for 1, 2 and 4 hours and 1100 °C for 0.5, 1 and 2 hours; (b) Mass gain of the AluChrom pre-treated at 800 °C, 900 °C, 1000 °C and 1100 °C for 1 hour.

Figure 1 shows the effect of pre-treatment temperature and time on the oxidation behaviour of the AluChrom 318. The mass increase obtained from pre-heat treatment corresponds to the reaction between oxygen and alloy elements which is mainly the establishment of an alumina layer in the case of an alumina-forming alloy. It can be clearly seen that the mass gain values increased with the pre-treatment temperature and time. The mass gain showed a linear relationship with the pre-treatment dwelling time while it had an exponential relation to the pre-heating temperature. Moreover, depending on the pre-treatment temperature, the slope of each linear relationship increased with the temperature. For samples pre-treated at the same temperature, the Al diffusion rate from the alloy base was constant for short-term pre-treatment, which resulted in the growth of alumina scale at a constant rate. Whereas, for the samples pre-treated for the same dwelling time but with varied temperatures, the exponentially increased Al diffusion rate at elevated temperature led to much more rapid growth of alumina on the surface (5).

The AluChrom 318 pre-treated at 800 °C, 900 °C, 1000 °C and 1100 °C for 1 hour were characterised by XRD to examine the effect of temperature on the alumina crystalline structure, and the obtained diffractograms are displayed in Figure 2. Peak

pattern matching of the XRD patterns showed the presence of Fe_2Nb for the samples pre-treated at all the four temperatures. For the samples pre-treated at 1000 °C and 1100 °C, XRD confirmed the formation of an $\alpha\text{-Al}_2\text{O}_3$ phase on the alloy surface. However, it is worth noting that the phase of alumina formed on the samples after being pre-treated at 800 °C and 900 °C could not be detected by XRD because the amount of alumina formed was too low and below the detection limit of the XRD technique.

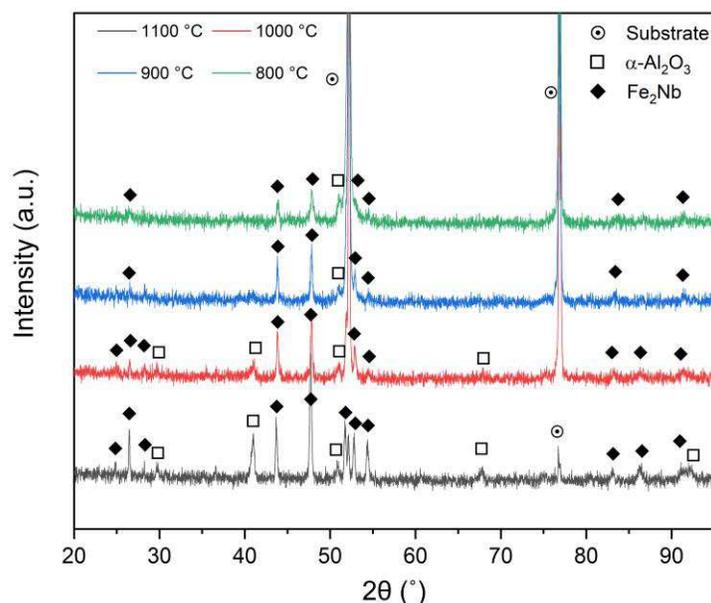


Figure 2. XRD patterns of the AluChrom 318 pre-treated at 800 °C, 900 °C, 1000 °C and 1100 °C for 1 hour.

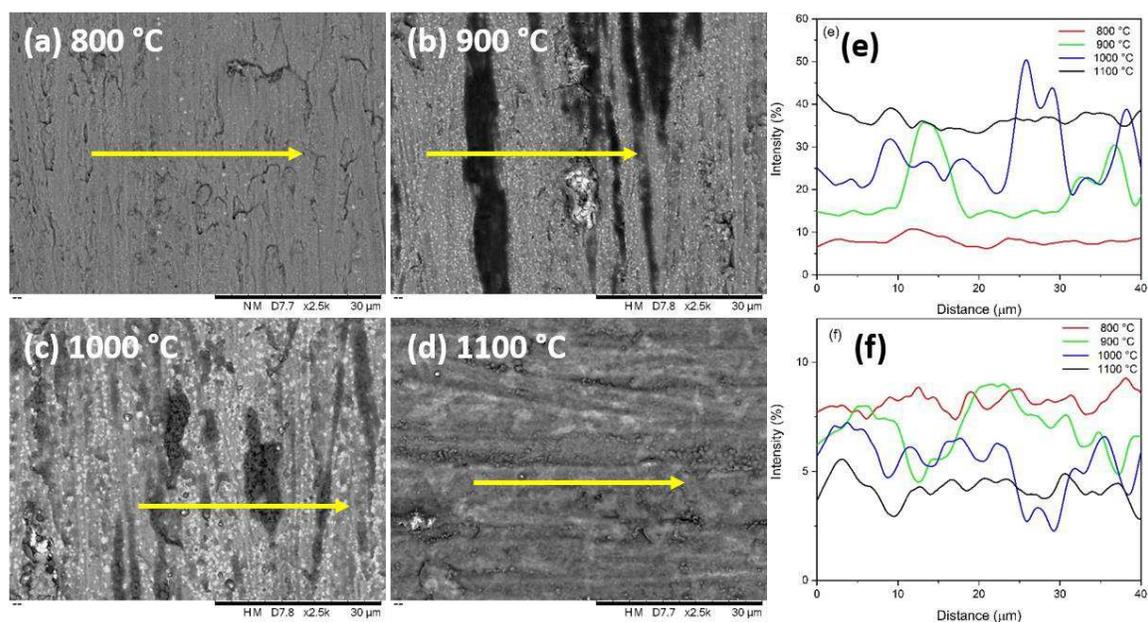


Figure 3. Backscattered electron images (BES) of the oxide scale formed after being pre-treated at 800 °C for 1 hour (a), at 900 °C for 1 hour (b), at 1000 °C for 1 hour (c) and at 1100 °C for 1 hour (d); EDX line scan of Al (e) and Cr (f) for the AluChrom 318 pre-heated at 800 °C, 900 °C, 1000 °C and 1100 °C for 1 hour along the line indicated in Figure 3a-d.

The SEM micrographs of all pre-treated samples are displayed in Fig. 3a-d. Fig. 3e and f compares the EDX line scan intensity of Al and Cr along the indicated line from the samples pre-treated for 1 hour at the four different temperatures. After pre-treatment at 800 °C, the surfaces still looked metallic, and the original scratches were still visible on the surface. As indicated by the EDX line scan, the surface of the AluChrom 318 after being treated at 800 °C for 1 hour exhibited the lowest intensity of Al and the highest intensity of Cr among all the 1-hour pre-treated samples. The samples pre-treated at 900 °C had built more alumina on the alloy surface compared to those pre-heated at 800 °C. However, the distribution of alumina on the surface was considered to be nonhomogeneous. As indicated by the EDX line scan for the sample pre-treated at 900 °C for 1 hour, the dark region showed extremely high intensity of Al and low intensity of Cr corresponding to the area covered with a thick alumina scale. In contrast, the grey region with lower intensity of Al and slightly higher intensity of Cr corresponded to the formation of a thinner alumina scale on the alloy surface. The alumina scale developed on the samples after being pre-treated at 1000 °C also had a nonhomogeneous thickness. However, the partially covered thick alumina formed on the samples pre-treated at 1000 °C exhibited a platelet-like structure which is completely different from that formed on the samples pre-treated at 900 °C. It should be noticed that the platelet-like alumina (Figure 3c) had a similar morphology to the γ -Al₂O₃ discovered by Kadiri *et al.* (6). The EDX line scan confirmed that the platelet-like alumina showed the highest intensity of Al and the lowest intensity of Cr. However, the thin alumina area in the sample pre-treated at 1000 °C for 1 hour still shows a lower Al intensity and higher intensity of Cr in comparison with the sample pre-heated at 1100 °C for 1 hour. Unlike the samples pre-heated at 900 °C and 1000 °C, the distribution of alumina scale on the samples pre-treated at 1100 °C was much more homogeneous with the highest intensity of Al and the lowest intensity of Cr. Furthermore, for the samples pre-treated at 1100 °C for 1 hour, the metastable alumina formed during the temperature ramping stage had dramatically reduced and the surface had been mostly covered with relatively dense and even α -Al₂O₃ layer. This can be explained by the fact that the 1100 °C used for pre-treatment promotes faster phase transformation of metastable alumina formed during the temperature ramping stage to the stable α -Al₂O₃ phase compared to the other lower temperatures used.

Exposure Test

The mass gain of the pre-treated samples after 500 hours exposure at 850 °C in 3% humidified air (6.0 L/min) compared with the non-treated sample is plotted in Figure 4. It can be clearly seen that all the pre-treated samples showed a decreased mass gain compared to the non-treated sample (0.130 mg/cm²) over the 500 hours exposure test. In this study, a low mass gain corresponds to a low oxidation rate for the pre-treated samples exposed to the simulated SOFC cathode conditions. The samples pre-treated at 800 °C for 1 hour showed the highest mass gain (0.072 mg/cm²) among all the pre-treated samples after 500 hours exposure while the mass gain was found to be dramatically decreased with the pre-treated samples when the dwelling time increased to 4 hours (0.035 mg/cm²) at the same pre-treatment temperature. By comparing the same dwelling time and varying the temperature, the samples pre-treated at 900 °C for 1 hour (0.059 mg/cm²) showed a lower mass gain than the samples 800 °C for 1 hour, and the samples pre-treated at 900 °C for 4 hours (0.027 mg/cm²) showed a lower mass gain than the samples pre-treated at 800 °C for 4 hour after the exposure tests. The overall mass gain of the samples pre-treated at 1100 °C for 30 minutes (3.36×10^{-3} mg/cm²) was

slightly lower than the samples pre-treated at 1000 °C for 4 hours (4.44×10^{-3} mg/cm²) after 500 hours exposure. The best corrosion resistance was observed for the samples pre-heated at 1100 °C for 1 hour (4.37×10^{-4} mg/cm²) with a 98% reduction of oxidation rate compared to the non-treated AluChrom 318 due to the formation of an α -Al₂O₃ layer. The higher mass gain for the samples pre-treated at 800 °C and 900 °C corresponds to a faster Al outward diffusion rate (corrosion rate) for the development of an alumina scale on the outer surface, in comparison with the sample pre-treated at 1000 °C and 1100 °C. It should be noted that a fast Al consumption rate will cause the exhaustion of the Al reservoir in the alloy base which will eventually result in material failure at an accelerated rate. In this work, one of the main objectives to carry out the pre-treatment for the AluChrom 318 was to decrease the Al oxidation rate and make the Al reservoir last longer in the CAPH application. Therefore, the sample pre-treated at 1100 °C for 1 hour with the lowest oxidation rate amongst all the tested pre-treated samples could potentially extend material life much longer for the CAPH application.

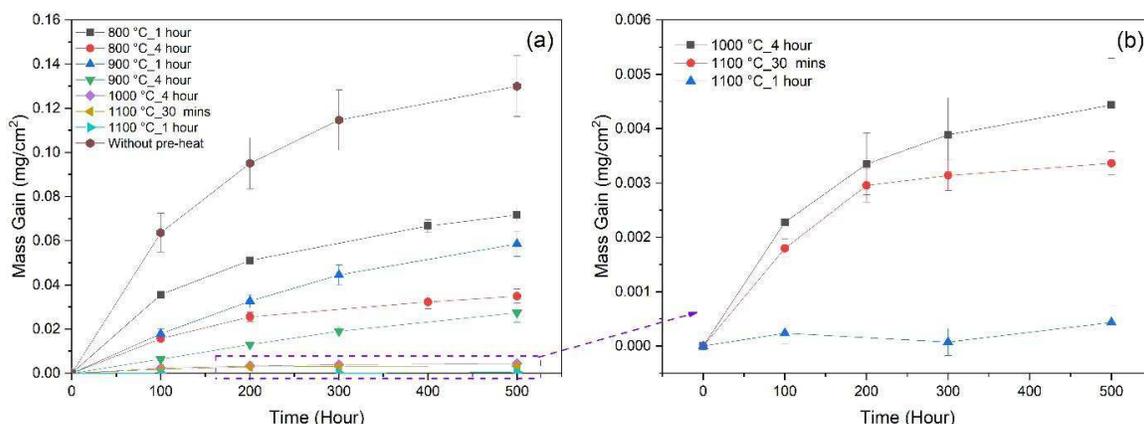


Figure 4. Discontinuous mass measurements of the non-treated and pre-treated AluChrom 318 exposed to 3 vol% humidified air (6.0 L/min) at 850 °C for 500 hours.

The evaporation of chromium from the treated and non-treated AluChrom 318 is plotted in Figure 5. It is interesting to note that the samples pre-treated at 800 °C for 1 hour showed the highest amount of Cr evaporation (6.37×10^{-3} mg/cm²). The higher Cr evaporation of the samples pre-treated at 800 °C for 1 hour compared to the non-treated samples is due to the fact that the formed Cr₂O₃ in the initial stage of pre-treatment cannot be completely covered by the simultaneously formed alumina scale under low pre-treatment temperature and short dwelling time conditions. Therefore, a large amount of Cr evaporation from the already built Cr₂O₃ is observed for the samples pre-treated at 800 °C for 1 hour. In contrast, the amount of Cr evaporated from the samples pre-treated at 800 °C for 4 hours (3.35×10^{-3} mg/cm²) was lower than the non-treated samples (5.62×10^{-3} mg/cm²) due to the increased surface coverage by alumina scale. The samples pre-heated at 900 °C for 1 hour had a similar level of Cr evaporation (3.38×10^{-3} mg/cm²) as those pre-heated at 800 °C for 4 hours. Whereas, with pre-treatment time increasing to 4 hours at 900 °C, the amount of Cr evaporated from the alloys had decreased to 1.98×10^{-3} mg/cm² which is 35% of that from non-treated samples. The samples pre-treated at 1000 °C showed an amount of Cr vaporisation of 2.26×10^{-3} mg/cm² which was comparable to that from the samples pre-treated at 900 °C for 4 hours. It is worth noting that the samples pre-heated at 1100 °C displayed the lowest level of Cr evaporation among all the pre-treatment temperatures investigated in this research. The quantity of Cr evaporated from the non-treated sample (5.62×10^{-3} mg/cm²) was 5 times higher than that

from the sample pre-treated at 1100 °C for 30 minutes (1.19×10^{-3} mg/cm²) and 10 times higher than that from the sample pre-treated at 1100 °C for 1 hour (6.07×10^{-4} mg/cm²) over the 168 hours of collection. The lowest mass gain and Cr evaporation which was achieved for the samples pre-treated at 1100 °C for 1 hour was due to the formed α -Al₂O₃ phase with a more compact lattice structure compared to the metastable alumina phase developed on the samples pre-treated at lower temperature.

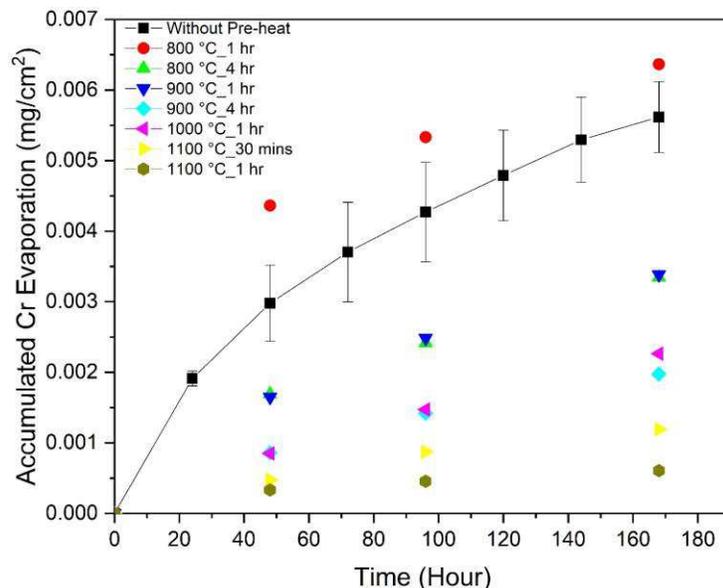


Fig. 5. Accumulated Cr evaporation as function of time for the non-treated and pre-heated AluChrom 318 exposed at 850 °C in 3 vol% humidified air for 168 hours.

Conclusions

The oxidation rate and Cr evaporation of the AluChrom 318 at 850 °C in humidified air was shown to be dramatically decreased by pre-treatment. It can be assumed that the kinetics of oxidation rate and Cr release for the pre-treated AluChrom 318 is governed by the phase formation of alumina on the alloy surface during pre-treatment. Pre-treatment at 800 °C and 900 °C resulted in less improvement in the oxidation resistance and Cr retention capability than at 1000 °C and 1100 °C due to the formed metastable alumina scale which allows relatively faster Al and Cr outward diffusion. The best corrosion resistance was observed for the samples pre-treated at 1100 °C for 1 hour (4.37×10^{-4} mg/cm²) with a 98% reduction of oxidation rate compared to the non-treated AluChrom 318 due to the formation of a compact and homogenous α -Al₂O₃ scale which can effectively prevent the Al and Cr from outward diffusion in the simulated SOFC environment. Thus, the samples pre-treated at 1100 °C for 30 minutes and 1 hour are considered to be promising pre-treatment conditions for industrial application for cost-effective processing.

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