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Method for Measuring Chromium Evaporation from SOFC Balance-of-Plant Components

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Cr poisoning is a well-identified performance degradation process in solid oxide fuel cells (SOFC). While stainless steel (SS) interconnects have been identified to be a significant source of Cr, the Cr contribution from balance-of-plant (BoP) components located upstream of the cathode still needs to be ascertained. A method to measure Cr concentration level from BoP components was developed in this work. The volatile Cr species were collected by air sampling through a quartz tube coated with sodium carbonate. SEM observations enabled to correlate changes in the oxide layer microstructure of BoP alloys to their Cr evaporation rate.

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Cr poisoning is a significant degradation process in solid oxide fuel cells (SOFC), limiting the lifetime of SOFC systems.[1–5] Sources of volatile Cr species are stainless steel (SS) components found in the balance-of-plant (BoP) and as metallic interconnectors (MIC). The volatile Cr species are carried in the air stream and deposit on electrochemically active cathode regions hence leading to performance degradation.

In the presence of humidity, the dominant species is Cr oxyhydroxide[6] which is formed according to Equation 1.

$$Cr_2O_3(s) + 2H_2O(g) + 3/2O_2(g) \rightarrow 2CrO_2(OH)_2(g) \quad [1]$$

MIC have been identified to be an important Cr source in current SOFC designs and solutions have been developed to mitigate Cr evaporation by using protective coatings.[7–9] Recently, BoP components have drawn attention as an additional Cr source.[10,11]

On the one hand, ferritic SS are used as MIC materials because of their low thermal expansion coefficient (TEC) mismatch with the common yttria-stabilized zirconia (YSZ) electrolyte material.[12] On the other hand, austenitic SS are preferred for high temperature components in the BoP of SOFC systems due to their better mechanical and corrosion properties. As BoP components, such as heat exchangers, exhibit more complex geometries involving complex manufacturing processes, Cr-evaporation barrier coatings developed for MIC are unsuitable for the BoP. Assessment of Cr evaporation rates from BoP components is therefore seen as a prerequisite for the development of solutions to reduce this effect, such as materials selection, surface treatment, coatings or Cr trapping,[13] as well as the evaluation of improvements brought by such solutions; an area where this work aims to contribute by a dedicated measurement technique.

Cr evaporation quantification is generally evaluated on small metal coupons,[7,9,14] wherefrom it is difficult to extrapolate the actual amount for a real, complex-shaped component (uneven temperature profile and large surface area), as the evaporation rate depends on several factors such as the flow rate, flow regime and (local) temperature. The present work focuses on the methodology development for direct quantification of volatile Cr in the hot gas stream of a BoP component, i.e. a SS pipe here. The presented method is based on the denuder-technique previously taken by Froitzheim et al.[9]

Silicon evaporation is not addressed here because its evaporation rate is five orders of magnitude lower than the Cr evaporation rate.[11]

Experimental

The experimental setup is schematically illustrated in Fig. 1. A 1.2 m long SS pipe (253MA, Sandvik, inner diameter 15.8 mm, composition available in ref. 15) was exposed to a high temperature in a furnace. Humidified air (1.8 vol-% H_2O) was fed into the pipe at a flow rate of 10 l_N/min. A quartz tube (diameter 5.2 mm and length 500 mm) was inserted into the steel pipe near its end. A fraction of the flow (15–35% of the main flow) was sampled through this quartz tube by a diaphragm pump and a rotameter. The inner wall of the quartz tube was dip-coated with sodium carbonate from a surfactant-containing solution. Equation 2 describes the reaction between sodium carbonate and volatile Cr species. According to HSC,[16] the equilibrium constant of equation 2 is above 10^{10} from ambient to 800°C.

$$CrO_2(OH)_2(g) + Na_2CO_3(s) \rightarrow Na_2CrO_4(s) + H_2O(g) + CO_2(g) \quad [2]$$

Each measurement lasted 24 hours, after which the coated quartz tube was replaced without cooling down the furnace, enabling repeated measurements. The coating was dissolved after sampling with 10% nitric acid, diluted to obtain a suitable Cr concentration, and analyzed by inductively coupled plasma mass spectrometry (ICP-MS, Thermo Scientific ELEMENT 2).

The effect of the SS pipe temperature on the Cr evaporation rate was investigated by triplicated Cr evaporation measurements, carried out at 650, 700 and 750°C.

The effect of the SS pipe's heat-treatment history on its Cr evaporation rate was also investigated. For this purpose, Cr evaporation measurements were carried out on a pipe at 750°C before and after an exposure to an elevated temperature of 800°C for 100 hours. Scanning electron microscopy and energy-dispersive X-ray spectroscopy (SEM and EDX, same as in Ref. 11) were used to investigate the correlation between microstructure and Cr evaporation rate.

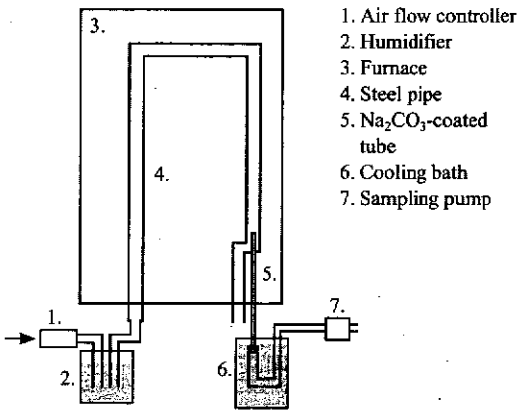

Figure 1. Schematic drawing of the experimental setup.

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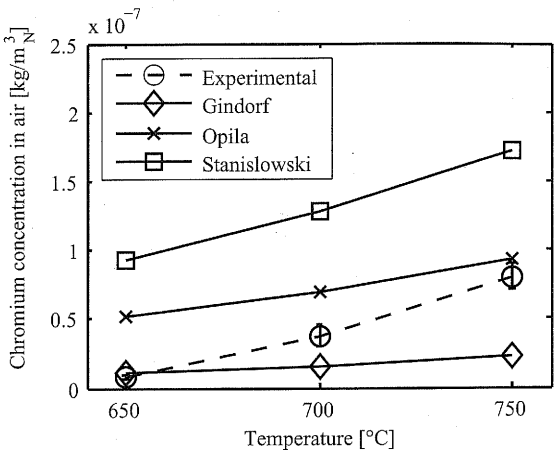

Figure 2. Measured amounts and standard deviations of evaporated Cr at different temperatures. The experimental data are compared with predictions based on thermodynamics data from different sources (data extracted from[7]).

Results and Discussion

In order to verify that most of the volatile Cr species react in the tube, coating dissolution was carried out in three steps, each corresponding to a third of the tube length. Only 7.3% of the total amount of Cr collected was found in the last third of the tube (the furthest from the Cr source), which indicates that the coated tube is sufficiently long for Cr collection. Another study found that a collection efficiency of 95% could be achieved in a similar setup.[9]

Systematic error was calculated to be 6% of the measurement (based on measurement accuracy and collection efficiency uncertainty). Random error is 13% (two times the standard deviation). The overall uncertainty is thus 14% (confidence level of 95%).

Effect of temperature on Cr evaporation.— Fig. 2 illustrates the results from Cr evaporation measurements at 650, 700 and 750°C, three measurements at each temperature, with predictions based on thermodynamics. These predictions are based on three different thermodynamics datasets extracted from.[7] The experimental values of Cr evaporation obtained with the method presented here are coherent with the literature and its good repeatability is demonstrated by the low standard deviations.

Effect of heat-treatment history on Cr evaporation:.— It was found that the temperature history has a significant effect on the amount of evaporated Cr at 750°C. Before the heat-treatment, the average volatile Cr concentration was 8.0×10^{-08} kg/m^3. After the heat-treatment (800°C, 100 hours), this value decreased to 2.0×10^{-08} kg/m^3 which corresponds to a reduction by a factor of 4. In order to explain the reason behind the decrease in Cr evaporation, SEM cross section and EDX elemental mapping were performed on the oxide layer before and after the heat-treatment. For this purpose, two SS pipes were both first exposed at a temperature of 750°C for Cr evaporation measurements. Additionally one pipe was exposed at 800°C for 100 hours before repeating Cr evaporation measurement at 750°C.

Fig. 3a and 3b show backscattered-electron (BSE) imaging of cross sections of the inner surface of the SS pipe before and after exposure at 800°C. Before exposure, a thin oxide layer (1 μm), mainly composed of Cr oxide is revealed by EDX (Fig. 3c). During exposure at 800°C, the scale has grown to 10 μm thickness; its outer oxide layer has become Cr depleted (Fig. 3d) and Fe oxide enriched (Fe EDX mapping not shown).

The reduction of Cr evaporation is explained by the growth of a thicker corrosion layer, which is Cr depleted at its surface. This Fe rich oxide layer formed during exposure at 800°C predicts a high

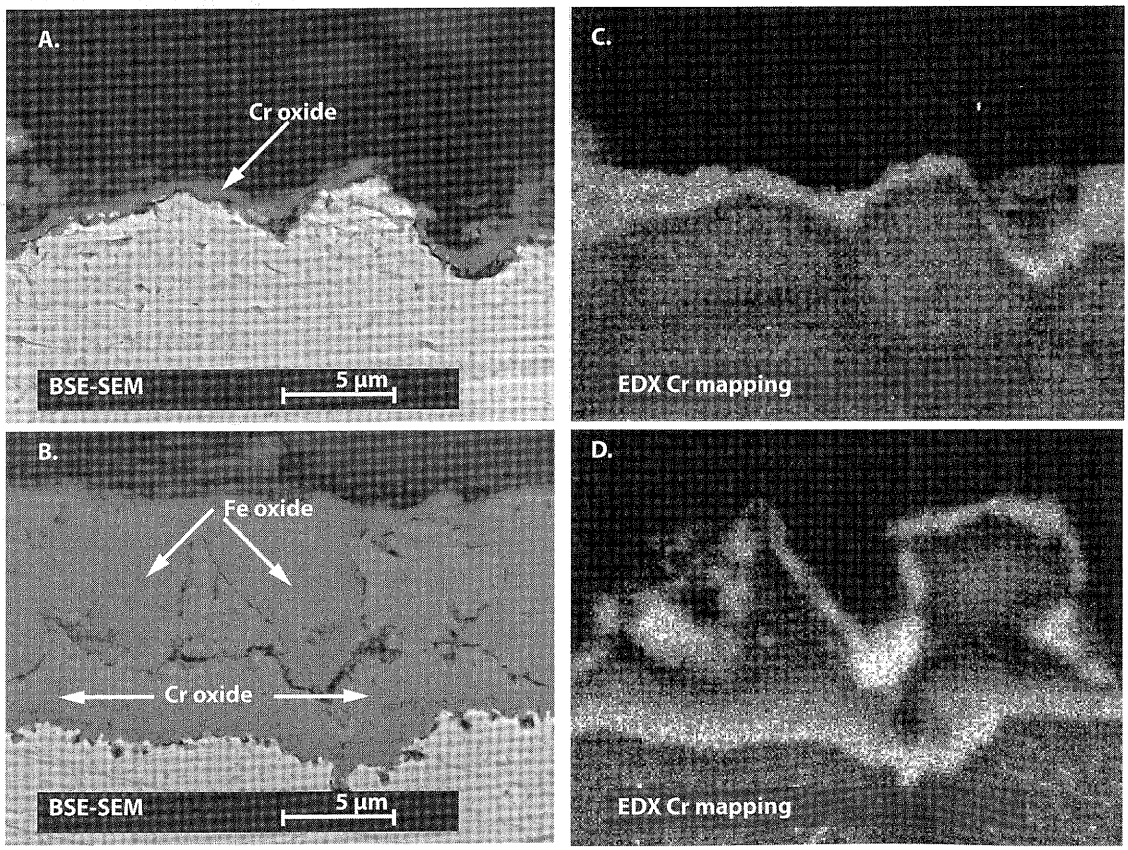

Figure 3. A. and B. SEM-BSE cross section of the SS before and after the 800°C heat-treatment. C. and D. EDX Cr mapping of the corresponding views.

corrosion rate and is thus not beneficial for SOFC applications despite a reduction of Cr evaporation by a factor 4.

Although the reason for the formation of such an oxide layer is not yet ascertained, this result is presented here to illustrate the ability of the Cr quantification method to notice an unexpected oxide layer growth through change in Cr evaporation rate. Alloy 253MA being designed to withstand higher temperature, this corrosion behavior is unexpected.

Conclusions

To gain insight on corrosion behavior of SOFC system components, a method to quantify Cr evaporation from BoP components was developed and evaluated on a heat-exchanger-imitating steel pipe.

The principle is to collect volatile Cr species by sampling hot air directly from a pipe (or any other BoP component) through a quartz tube coated with sodium carbonate. The coating is then dissolved and its Cr content analyzed by ICP-MS.

The experimental assembly is robustly designed in a way that enables its implementation at various places within a SOFC system. This makes possible the assessment of local Cr concentrations, such as at the stack air inlet or exhaust location, or after BoP components suspected to be a significant Cr source. Hence, the method enables identification of the major Cr sources of the system.

The method presented was sensitive enough to detect a heat-treatment induced decrease in evaporation rate caused by an oxide scale growth. The precision and repeatability of this measurement technique being proven, it will be used to quantify Cr evaporation from a stainless steel heat exchanger in system-relevant conditions.

Acknowledgments

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