

MODELLING OF CHROMIUM CONTAMINATION OF SOFC CATHODES FROM METALLIC INTERCONNECTS

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ABSTRACT

Solid oxide fuel cells, SOFCs, offer excellent environmental performance compared to power generation technologies that rely on combustion. Intermediate temperature solid oxide fuel cells stacks operating at 600-800°C may enable the use of inexpensive metallic alloys as interconnect material. In the last decade for this purpose ferritic steels with high contents of chromium are designed and investigated. Against their implementation however is the evaporation of chromia, formed on the interconnect surface at high temperature and preventing it from corrosion. The volatile Cr-species penetrate into the ceramic cathode from solid phase and block the active sites where oxygen is reduced, thus worsening the stack performance. The aim of this study is a modeling of the transport process in gas phase from the IC to the cathode surfaces. In first approximation it is divided into diffusion and flow drift. The diffusion coefficient of the prevailing species are estimated according to the kinetic gas theory. Calculation of the amount of Cr reaching the cathode is done for interconnect channels with square cross section in a planar SOFC stack, on the basis of thermodynamically treated evaporation process.

Keywords: SOFC, metallic IC, Cr-evaporation, transport in gas channels, cathode contamination.

INTRODUCTION

Solid oxide fuel cells (SOFCs) are fundamentally more efficient than combustion systems because they make energy electrochemically, and do not burn fuel. SOFC can have multiple geometries. The planar geometry is the typical sandwich type geometry employed by most types of fuel cells, where the electrolyte is sandwiched in between the electrodes. To achieve the required power individual cells are united into stacks with interconnects (IC).

In the past decade ferritic chromium steels are regarded as promising candidate materials for interconnect applications in intermediate-temperature planar solid oxide fuel cell (SOFC) stacks. High

temperature materials in technical applications rely on the protective effect of oxide scales. If there were not such dense and intact surface oxide scales on high temperature alloys, formed during service unimpeded internal corrosion attack would be possible. Ferritic steels with high Cr-contents are covered by a dense layer of chromia, which prevent further corrosion and determine their rather high oxidation resistance as well as the thermal expansion match to the other stack components, alongside with the fulfillment of the important requirements for gas impermeability and good electron conductance. Nevertheless, according to some researchers [1-4] uncertainties remain in their long-term surface stability and electrical resistance arising from the oxide scale growth, as well as chromia evaporation,

the species of which form solid phase and block the active sites in the cell cathode, where oxygen reduces, thus leading to the stack deterioration.

The aim of the present paper is to estimate the amount of Cr reaching the cathode from the evaporated Cr-species in the interconnect channels.

CALCULATIONS

The task is divided into three subtasks: (i) using thermodynamic software to calculate the partial pressure of Cr-species in the gas channel; (ii) on a basis of a model to estimate the portion of it, that is carried away by the air flux in the channel, and consequently the fraction, reaching the cathode; (iii) calculation of the diffusion coefficient of Cr(VI)-species into air.

Partial pressures of Cr-species over steel at high temperature in oxygen atmosphere

The vaporization of solid Cr_2O_3 in oxygen containing atmospheres – dry and humid air – in contact with the cathode and the IC, according to [5-7] produces sequences of oxides, hydroxides and oxihydroxides in which Cr is in different oxidized states, i.e. CrO_i , where $i=0,1,2,3$; Cr(OH)_j , where $j = 1, \dots, 6$; CrO(OH)_k , where $k=1, \dots, 6$ and $\text{CrO}_2(\text{OH})_l$, $l=1,2$.

A promising approach is to predict the possibility of the formation reactions using Gibbs energy of formation, and then from kinetic consideration to detail how the processes will take place as a function of time. Several thermodynamic database can be used nowadays, e.g. [8-10]. The choice of primary data must be done carefully [11], as the results of the calculations depend on: (i) reliable fundamental data, obtained by critical assessment and experiments; (ii) reliable models to represent the thermodynamic functions for the

phases and (iii) reliable computer codes to perform the calculations. Information is required about data acquisition and which reference state is used.

The reported results below are obtained using software package Chemical Workbench with integrated database Carat [12]. The compilation of tables prepared by Gurvich et al. [9] (also referred as IVTAN - the Institute for High Temperatures of the USSR Academy of Sciences) contain thermodynamic values for the oxides, hydrides oxihydroxides of Cr in their standard state. The data for the gases are quoted over the temperature range comprising that of interest 400 –1500 K. All of the experimental data have been recalculated on the basis of critically selected thermodynamic constants, and as a result, total internal consistency is quoted for all the tabulated thermodynamic functions and the accepted values of the thermo chemical constants. The obtained partial pressures, some of which are shown in table 1 permit the identification of the most abundant species as CrO_3 and $\text{CrO}_2(\text{OH})_2$.

Transport in the air channel

The geometry of the interconnect channel is depicted in Fig. 1.

IC-channel has square cross section. From its sides – two perpendicular and one –parallel to the cathode, volatile Cr-species are released which reach the cathode by diffusion gas in gas. A fraction of them is however carried away by the air flow with velocity w through the channel.

For the calculation of the fraction of the Cr-species carried away with the outlet gas several approximations are made:

(i) The Cr-species, arrived at $Z=h$ (h is the height of the channel) immediately vanish into the cathode (perfect deposition conditions or “trap”-model)

Table 1. Partial pressures of the Cr-species in air IC channel as a function of temperature.

T/K	SUM P/Pa	P(CrO_3)/Pa	P CrO(OH)_2 /Pa	P $\text{CrO}_2(\text{OH})_2$ /Pa
800	6.1×10^{-06}	8.7×10^{-09}	2.8×10^{-14}	6.1×10^{-06}
850	1.2×10^{-05}	7.4×10^{-08}	2.9×10^{-13}	1.2×10^{-05}
900	2.2×10^{-05}	4.9×10^{-07}	2.3×10^{-12}	2.2×10^{-05}
950	3.9×10^{-05}	2.7×10^{-06}	1.5×10^{-11}	3.7×10^{-05}
1000	7.2×10^{-05}	1.2×10^{-05}	8.2×10^{-11}	6.0×10^{-05}
1050	1.4×10^{-04}	4.8×10^{-05}	3.7×10^{-10}	9.3×10^{-05}
1100	3.0×10^{-04}	1.7×10^{-03}	1.5×10^{-09}	1.3×10^{-04}
1150	7.2×10^{-04}	5.2×10^{-03}	5.3×10^{-09}	2.0×10^{-04}

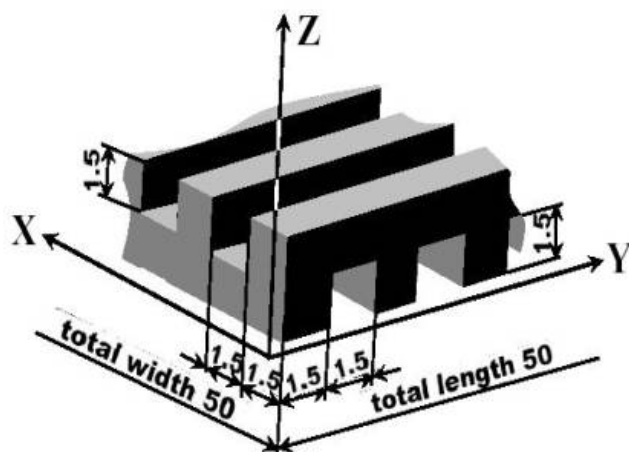


Fig. 1. Schematic representation of an IC section with the dimensions – width, height and length of the air channel in mm [7].

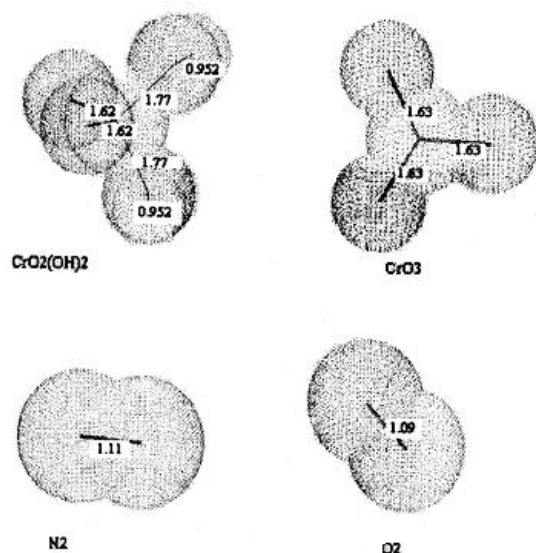


Fig. 2. Optimized geometries of the molecules; bond lengths are specified.

Table 2. Effective radius of molecules.

molecule	N ₂	O ₂	CrO ₃	CrO ₂ (OH) ₂
Radius/Å	1.603	1.599	2.791	2.916

(ii) the problem is regarded as one-dimensional – i.e. Cr is released only from the opposite to the cathode side of the interconnect. This approximation leads to an overestimation of the fraction of chromium carried away with the outlet gases.

(iii) The diffusion is treated as stationary, which is true after establishing of the stationary state. If a three-dimensional coordinate system is associated with the channel, as it is shown in Fig. 1, the concentration C is constant for every X and Y .

(iv) Cr-species diffuse with diffusion coefficient D_{ij} according to Fick's law, by its integration at conditions $Z = h$, $C = C_0$ and $Z = 0$, $C = 0$ one obtains $C = C_0 Z/h$.

(v) The gas flow is assumed incompressible, inviscid, laminar and steady with a rate w_x . These approximations follow from the working conditions.

For the estimation of the trapped into the cathode amount of Cr per seconds, ρ (mol/s) the diffusion coefficient of Cr-species in air is needed. It can be calculated if the molecules are approximated with spheres of known radii.

Diffusion coefficient of Cr (VI)-species in air

With the aid of software program HyperChem v.7 [13] by semi-empirical quantum chemical methods the optimized geometry of the gases is calculated and is shown in Fig 2. For the purpose two methods were applied: AM1 (Austin Model 1) for nitrogen and oxygen molecules, and - PM3 (Parametric Model number 3)- for Cr(VI)-species.

The effective radius is obtained as radius of the sphere around the corresponding molecule (see table 2).

The diffusion coefficient is calculated according the gas theory with the equation of Maxwell-Stepfan [14]:

$$D_{ij} = \frac{1}{3P\sigma_{ij}^2} \left(\frac{k_B T}{\pi} \right)^{1.5} \left(\frac{8}{\mu} \right)^{0.5},$$

where σ is the collision cross section radius, calculated as sum of the effective radii of the colliding molecules (the radius of the “air” molecule is an weighted value of the radii of the oxygen and nitrogen molecules) and μ is reduced mass, P is the total pressure.

At 850°C the obtained value for the diffusion coefficient is $8,46 \cdot 10^{-5} \text{ m}^2 \text{ s}^{-1}$. Using the above value of the diffusion coefficient and taking into account the linear velocity w_x of the air in the channel it was possible to calculate mass fluxes in X and Z directions:

$$\dot{n}_z = SD_{i,j} \frac{C_o}{l}$$

$$\dot{n}_x = A \cdot w_x \frac{C_o}{2} \quad ,$$

where S being the area of the cathode exposed to one channel and A – the cross section of the channel, which permits the evaluation of the fraction of the Cr(VI)-species trapped by the cathode. The calculations at 850°C and with $w_x = 1 \text{ m/s}$ yield 74%; the absolute value of the rate of Cr-penetration into the cathode is equal to $1,73 \cdot 10^{-13} \text{ mol/s}$. For an exploitation period of 1000 h this gives for the Cr-amount in the cathode $43 \cdot 10^{-6} \text{ g/cm}^2$.

The validation of the proposed approach and the obtained diffusion coefficient is made by a comparison with literature data [15]. The measured quantity of Cr by the transpiration method is $2,2 \cdot 10^{-10} \text{ kg m}^{-2} \text{ s}^{-1}$. Re-calculated data gives a good coincidence: $79 \cdot 10^{-6} \text{ g/cm}^2$.

CONCLUSIONS

A simple procedure for estimating of the Cr-amount deposited into the cathode under working conditions (temperature, relative humidity, % Cr in the steel) and consequent life time prediction is proposed. The procedure is developed in case of planar anode supported cells (ASC) using standard LSM cathode and YSZ electrolyte. Verification and comparisons are done with the experimental data obtained mainly by researcher in Forschung Zentrum Juelig (FZJ).

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