

# Modelling SOFC steel interconnect chromium oxide layer growth

## 2NP Mini Project 3

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### Abstract

A model was derived for the growth of a protective chromium oxide layer on the air-steel boundary of a steel interconnect in a solid oxide fuel cell. Due to time constraints, this model could not be successfully implemented and did produce useful results.

## 1 Introduction

Solid oxide fuel cells (SOFCs) are a type of fuel cell characterised by having a solid oxide layer or ceramic electrolyte[3]. They can be used to power residential buildings and businesses; they are relatively low cost and the energy wasted by high running temperatures can be used for heating. They can also be used as backup power in transportation, and to store excess energy on the grid[1].

Technical advances that reduce the operating temperature of SOFCs will enable less expensive materials like steel to be used for internal components.

In this report we analyse the growth of a chromium oxide layer on an SOFC made out of steel containing chromium. The steel interconnect is used to connect adjacent fuel cells together. One side of the steel interconnect is in contact with a layer of air; the chromium in the steel reacts with oxygen in the air to form a layer of chromium oxide (chromia).

This chromia layer grows as more chromium diffuses (through the steel then through the existing chromia layer) to the chromia-air boundary surface to react with oxygen in the air and form more chromia. However, the chromia also reacts with water in the air, causing it to evaporate.

The chromia layer protects the steel from oxidation (which would cause damage to the steel and reduce its lifespan), but significantly increases the resistance of the interconnect; this has a significant effect on the efficiency of the SOFC since all current must flow the interconnect.

A chromia layer thickness of  $1\mu\text{m}$  is considered optimal. Companies developing commercial SOFCs require that the steel interconnect have a lifespan of at least 100,000 hours. We will determine a model for the thickness of the chromia

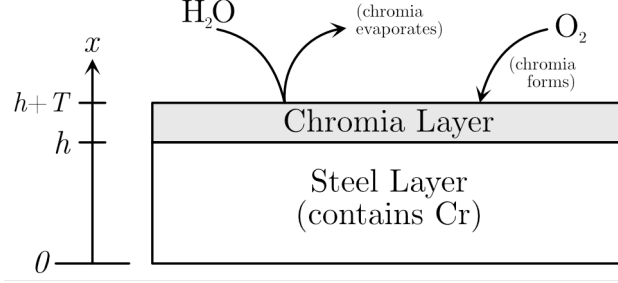


Figure 1: Steel interconnect modelled as having uniform chromium concentration  $C_{Cr}(x, t)$  at depth  $x$ .

layer and discuss how the design of the interconnect or fuel cell could be adapted to keep the thickness of the chromia layer to as close to  $1\mu m$  as possible for as long as possible.

## 2 Method

### 2.1 Model

Figure 1 shows a diagram of the model. We model the interconnect as a perfect rectangle with uniform concentration  $C_{Cr}(x, t)$  at depth  $x$  through the interconnect (as measured from the bottom surface opposite the chromia layer) after time  $t$ . We model the chromia layer as having uniform thickness  $T(t)$  after time  $t$ .

We model the chromia layer as having uniform thickness  $T(t)$  after time  $t$  (seconds). We model the interconnect as a perfect rectangle with uniform concentration  $C_{Cr}(x, t)$  at depth  $x$  (cm) through the interconnect (as measured from the bottom surface opposite the chromia layer) after time  $t$ .

Let:

- $h = 0.0508\text{cm}$  be the initial thickness of the steel interconnect.
- $D_c = 7.30 \times 10^{-15}\text{cm}^2\text{s}^{-1}$  be the diffusion coefficient of chromium through the chromia layer.
- $D_s = 2.00 \times 10^{-10}\text{cm}^2\text{s}^{-1}$  be the diffusion coefficient of chromium through the steel interconnect.
- $C_{wa} = 3\%$  be the concentration of water in the air.
- $k_1$  be the rate of the oxidation reaction.
- $k_2$  be the rate of the evaporation reaction.

The growth of the oxide layer is described by the differential equation

$$\frac{\partial T}{\partial t} = f(t, T(t), C_{\text{Cr}}(h, t)) = \frac{k_1 C_{\text{Cr}}(h, t)}{1 + (k_1 T / D_c)} - k_2 C_{\text{wa}} \quad (1)$$

which depends on the concentration  $C_{\text{Cr}}(h, t)$  of chromium at the chromia-steel layer boundary. So, we also have to solve the concentration  $C_{\text{Cr}}$ , which is described by the equation

$$\frac{\partial C_{\text{Cr}}(x, t)}{\partial t} = D_s \frac{\partial^2 C_{\text{Cr}}(x, t)}{\partial x^2}. \quad (2)$$

We will proceed by using Euler's method for (1) and an FTCS scheme for the concentrations, both with a time step of  $\Delta t$ .

## 2.2 Discrete Intervals

We first discretise the  $x$  axis into  $N$  intervals of equal width  $\Delta x = \frac{h}{N}$  using  $N + 1$  points  $x_0, x_1, \dots, x_N$  with  $x_i = i(\Delta x)$ .

Denote  $C_i(t) = C_{\text{Cr}}(x_i, t)$ , and define vector  $C(t) = (C_0(t), C_1(t), \dots, C_N(t))$  to contain the concentrations at the  $x$  points at each time value.

## 2.3 Solving $T$

Using Euler's method for (1) we obtain

$$T(t + \Delta t) = T(t) + (\Delta t)f(t, T(t), C_{\text{Cr}}(h, t)).$$

## 2.4 FTCS Scheme

We use the Euler's method approximation to obtain

$$\frac{\partial C_{\text{Cr}}(x, t)}{\partial t} = \frac{C_{\text{Cr}}(x, t + \Delta t) - C_{\text{Cr}}(x, t)}{\Delta t}$$

and a central difference approximation to obtain

$$\frac{\partial^2 C_{\text{Cr}}(x, t)}{\partial x^2} = \frac{C_{\text{Cr}}(x + \Delta x, t) - 2C_{\text{Cr}}(x, t) + C_{\text{Cr}}(x - \Delta x, t)}{(\Delta x)^2}.$$

Equation (2) thus gives

$$\frac{C_{\text{Cr}}(x, t + \Delta t) - C_{\text{Cr}}(x, t)}{\Delta t} = D_s \frac{C_{\text{Cr}}(x + \Delta x, t) - 2C_{\text{Cr}}(x, t) + C_{\text{Cr}}(x - \Delta x, t)}{(\Delta x)^2}$$

which rearranges to

$$C_{\text{Cr}}(x, t + \Delta t) = \delta C_{\text{Cr}}(x + \Delta x, t) + (1 - 2\delta)C_{\text{Cr}}(x, t) + \delta C_{\text{Cr}}(x - \Delta x, t)$$

with

$$\delta = \frac{D_s \Delta t}{(\Delta x)^2}.$$

Using our discretised grid points,

$$C_i(t + \Delta t) = \delta C_{i+1}(t) + (1 - 2\delta)C_i(t) + \delta C_{i-1}(t). \quad (3)$$

This equation describes a FTCS scheme with time step  $\Delta t$ . The boundary points  $C_0(t)$  and  $C_N(t)$  cannot be calculated using Equation 3 since  $C_{-1}(t)$  and  $C_{N+1}(t)$  do not exist. We need boundary conditions.

## 2.5 Boundary Conditions

### 2.5.1 Bottom: $C_0(t)$

On the underside of the steel interconnect we must have that flux  $J$  is 0. This is because no chromium is entering or exiting the interconnect on this side (this is an assumption of the model - if there was another air layer below the model would need to be modified); the rate of matter flow per unit area (flux) must be 0. Thus,

$$0 = J(x = 0, t) = -D_s \frac{\partial C_{Cr}(0, t)}{\partial x}.$$

Since  $D_s \neq 0$  (this would mean chromium would not diffuse at all), we must have

$$\frac{\partial C_{Cr}(0, t)}{\partial x} = 0,$$

i.e.

$$\frac{\partial C_0(t)}{\partial x} = 0 \quad (4)$$

using our discrete points.

We enforce this Neumann boundary condition using a false point as described in Section 3.2.3 of [4]. We introduce an external false point  $x_{-1} = x_0 - \Delta x = -\Delta x$  and corresponding concentration  $C_{-1}(t) = C_{Cr}(-\Delta x, t)$ .

Using a central difference approximation,

$$0 = \frac{\partial C_0(t)}{\partial x} \approx \frac{C_1(t) - C_{-1}(t)}{2\Delta x}$$

Thus,

$$C_{-1}(t) = C_1(t)$$

Now that we know  $C_{-1}(t), C_0(t), C_1(t)$  we can apply our FTCS scheme (3) to find  $C_0(t + \Delta t)$ .

$$\begin{aligned} C_0(t + \Delta t) &= \delta C_1(t) + (1 - 2\delta)C_0(t) + \delta C_{-1}(t) \\ &= 2\delta C_1(t) + (1 - 2\delta)C_0(t). \end{aligned}$$

### 2.5.2 Top: $C_N(t)$

We approximate the concentration through the chromia layer as a linear function of the concentration at the chromia-steel boundary face ( $x = h + T$ ) to obtain

$$\left. \frac{\partial C_{\text{Cr}}(x, t)}{\partial t} \right|_{x=h+T} = \frac{k_1 C_{\text{Cr}}(h, t)}{1 + (k_1 T / D_c)} = \frac{k_1 C_N(t)}{1 + (k_1 T / D_c)} = g(t, T(t), C_N(t)) \quad (5)$$

Let  $C_{\text{surf}}(t)$  be the concentration of chromium at the surface of the chromia layer. So

$$C_{\text{surf}}(t) = C_{\text{Cr}}(h + T(t), t).$$

Equation 5 becomes

$$\frac{\partial C_{\text{surf}}(t)}{\partial t} = g(t, T(t), C_N(t)).$$

If the concentration through the chromia layer is approximately linear, the concentration gradient will be constant w.r.t.  $x$  and equal to

$$\frac{\partial C_{\text{Cr}}}{\partial x} = \frac{C_{\text{surf}}(t) - C_{\text{Cr}}(h, t)}{T}$$

When  $T = 0$ , we define  $\frac{\partial C_{\text{Cr}}}{\partial x} = 0$  (for our purposes,  $C_{\text{surf}}(t) = C_{\text{Cr}}(h, t)$  whenever  $T = 0$ ).

We assume that the concentration  $C_{\text{Cr}}(x, t)$  is continuous on  $x \in [0, h + T]$  and at point  $x = h$  in particular. We want a boundary condition for the chromium in the steel; at  $x = h$ ,

$$\begin{aligned} \frac{\partial_- C_{\text{Cr}}}{\partial x} &= \frac{D_c}{D_s} \frac{\partial_+ C_{\text{Cr}}}{\partial x} \\ &= \frac{D_c}{T D_s} (C_{\text{surf}}(t) - C_{\text{Cr}}(h, t)) \\ &=: Q(t, T(t), C_{\text{surf}}(t), C_N(t)) = Q(t) \end{aligned}$$

Note: we're expecting that  $C_{\text{surf}}(t) < C_{\text{Cr}}(h, t)$  so that  $Q(t) < 0$ .

We use Euler's method to calculate  $C_{\text{surf}}(t)$ . Since  $T(0) = 0$ , we use initial condition  $C_{\text{surf}}(0) = C_{\text{Cr}}(h + T, t = 0) = C_{\text{Cr}}(h, 0) = 0.26$ . Then

$$C_{\text{surf}}(t + \Delta t) = C_{\text{surf}}(t) + \Delta t \cdot g(t, T(t), C_N(t))$$

Our boundary condition is

$$\frac{\partial C_N(t)}{\partial x} = Q(t)$$

To enforce this, we again introduce an external false point  $x_{N+1} = x_N + \Delta x$  and corresponding concentration  $C_{N+1}(t) = C_{Cr}(h + \Delta x, t)$ .

Using a central difference approximation,

$$Q(t) = \frac{\partial C_N(t)}{\partial x} \approx \frac{C_{N+1}(t) - C_{N-1}(t)}{2\Delta x}$$

so

$$(2\Delta x)Q(t) + C_{N-1}(t) = C_{N+1}(t).$$

Finally we apply our FTCS scheme (3) to obtain

$$\begin{aligned} C_N(t + \Delta t) &= \delta C_{N+1}(t) + (1 - 2\delta)C_N(t) + \delta C_{N-1}(t) \\ &= \delta((2\Delta x)Q(t) + C_{N-1}(t)) + (1 - 2\delta)C_N(t) + \delta C_{N-1}(t) \\ &= (1 - 2\delta)C_N(t) + 2\delta C_{N-1}(t) + R(t) \end{aligned}$$

where

$$\begin{aligned} R(t) &= 2\delta(\Delta x)Q(t) \\ &= 2\frac{D_s\Delta t}{\Delta x}Q(t) \\ &= 2\frac{D_s\Delta t}{\Delta x}\frac{D_c}{TD_s}(C_{\text{surf}}(t) - C_N(t)) \\ &= \frac{2D_c\Delta t}{T\Delta x}(C_{\text{surf}}(t) - C_N(t)). \end{aligned}$$

## 2.6 Concentration Computation

Our final concentration computation is therefore given

$$C(t + \Delta t) = A \cdot C(t) + B$$

with

$$A = \begin{pmatrix} (1 - 2\delta) & 2\delta & 0 & \cdots & 0 & 0 \\ \delta & (1 - 2\delta) & \delta & \ddots & \vdots & \vdots \\ 0 & \delta & (1 - 2\delta) & \ddots & 0 & 0 \\ \vdots & \ddots & \ddots & \ddots & \delta & 0 \\ 0 & \cdots & 0 & \delta & (1 - 2\delta) & \delta \\ 0 & \cdots & 0 & 0 & 2\delta & (1 - 2\delta) \end{pmatrix}$$

and

$$B = \begin{pmatrix} 0 \\ \vdots \\ 0 \\ R(t) \end{pmatrix}.$$

## 2.7 Initial Conditions and summary

We have the following initial conditions for  $t = 0$ :

- $T(0) = 0$  (there's no initial oxide layer)
- $C_i(0) = 0.26$  (concentration starts at 26%)
- $C_{\text{surf}}(0) = 0.26$

At a given time step  $t$  we do the following:

1. Calculate  $T(t + \Delta t)$  using Euler's method:

$$T(t + \Delta t) = T(t) + (\Delta t)f(t, T(t), C_N(t)).$$

2. Calculate  $C_{\text{surf}}(t + \Delta t)$  using Euler's method:

$$C_{\text{surf}}(t + \Delta t) = C_{\text{surf}}(t) + \Delta t \cdot g(t, T(t), C_N(t)).$$

3. Calculate vector  $C(t + \Delta t)$  using our FTCS scheme:

$$C(t + \Delta t) = A \cdot C(t) + B$$

Where  $B$  depends on  $T(t)$ ,  $C_{\text{surf}}(T)$ , and  $C_N(t)$ ; the order of these steps is thus important.

## 2.8 Stability

By Von Neumann analysis it can be determined that our FTCS scheme is stable if and only if  $\Delta t$  satisfies the relationship:

$$\Delta t \leq \frac{\Delta x^2}{2D_s}.$$

Since we want  $\Delta t$  to be as large as possible to minimise the required computation, we set

$$\Delta t = \frac{\Delta x^2}{2D_s}.$$

### 3 Results

The above method was implemented as a python script. Unfortunately, the model did not produce meaningful results. Regardless of the parameters used, the chromia layer thickness  $T$  increased initially and then dropped rapidly to large negative values.

The model was modified in various ways in an attempt to produce reasonable output. Unfortunately, none of these were successful. It's likely that this issue was caused by an underlying flaw in the mathematics of the top boundary condition on the FTCS scheme.

### 4 Discussion

If the model had solved the oxide growth problem successfully, a parameter analysis could have been performed on  $k_1$  and  $k_2$ . These rates of reaction would depend heavily on the running temperature of the fuel cell; our oxide-layer model could have been used to predict the lifespan of the steel interconnect for different operating temperatures.

The thickness and initial concentration level of the steel interconnect could also have been analysed to determine which design parameters would keep the thickness of the chromia layer close to  $1\mu\text{m}$  for the longest, thus maximising the lifespan of the steel interconnect.

Part (b) of the problem brief asks us to determine the amount of mass gain for different rate parameters to see which parameters match up to observed mass gain measurements and could therefore be plausible values.

This part of the problem was not attempted due to time constraints. However, both the mass lost and mass gained could be solved using Euler's method in a similar way to that used in the method described above.

### 5 Conclusion

A mathematical model for solving the oxide growth problem numerically was developed. Due to time constraints, the method could not be successfully implemented. If it had been, it could have been useful to determining design characteristics of the fuel cell and interconnect that would maximise the lifespan of the steel interconnect.

There may be a fundamental flaw in the mathematics of the method described, particularly in the top boundary condition of the FTCS scheme. Although no such flaw was found, this should be investigated further.

### References

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