MODELING AN H$_2$S FED SOFC

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ABSTRACT

We present models we have built for a single H$_2$S fuelled SOFC. The cell is a planar cell with a circular disc-like electrode assembly and the fuel and air flow through a concentric cylindrical tube assembly. The goal is to model the electrochemical reaction coupled with mass transfer, fluid flow and current/voltage distribution in an yttria stabilized zirconia electrolyte fuel cell assembly operated between 750 and 850°C. The models built range in complexity from an algebraic system of equations that calculates the activation, concentration and ohmic losses, to a 2-dimensional finite element model that solves all the physics in the SOFC simultaneously. The models are validated against experimental data (current density - cell voltage curves) both with and without IR compensation.

INTRODUCTION

Hydrogen sulphide (H$_2$S) is a by-product of the natural gas and the petrochemical industries. In addition to being toxic to most forms of life it is an unpleasant smelling air pollutant. The primary industrial process used to dispose off H$_2$S is the Claus process. The Claus process converts the gaseous H$_2$S to sulphur, a solid at ordinary temperatures, using a fairly complicated multistage process that has high operating costs.

If H$_2$S can be used as fuel in a fuel cell, it can be disposed off in a much simpler process that generates high quality electrical energy. The earliest studies on the possibility of using H$_2$S in a fuel cell were conducted by Pujare and coworkers (1). Since then a number of studies have been published on SOFCs running on H$_2$S (2, 3). These studies were experimental ones that evaluated different materials for the anode, anode catalysts, and electrolyte. The goal of these studies was to find materials that lead to stable performance for H$_2$S fuel cells without degradation over time.

There are two possible overall reactions that can use H$_2$S directly in a fuel cell:

\[ H_2S + \frac{1}{2}O_2 \Leftrightarrow H_2O + \frac{1}{2}S_2 \]  
\[ H_2S + \frac{3}{2}O_2 \Leftrightarrow H_2O + SO_2 \]

At the operating temperatures of a SOFC, these reactions are equally favoured thermodynamically and thus produce equilibrium voltages that are very close to each other e.g., 0.782 V for the first and 0.75 V for the second at 800°C (4). Besides these
reactions, part of the H₂S fed dissociates into H₂ and S₂ and these can then undergo electrochemical oxidation. It is not yet fully clear which (if any) of these reactions predominates in a SOFC running on H₂S (5, 4).

MODELING

As with any fuel cell system, SOFCs can be modelled on many levels. Models have been built at the electrode, single cell, and cell stack levels. The earliest studies by Debendetti and Vayenas (6) were on the single cell level. This model was later extended to model a layer of cells in a cross-flow stack (7). These models were 2-D in nature and only modelled the average concentrations and temperature in each cell in the stack layer, while ignoring mass transfer and electrochemical kinetics. Since these studies, a large number of models with increasing levels of complexity and detail have been built, and a good review can be found in chapter 11 of Singhal and Kendall (8).

In this work, we are modelling the fuel cell investigated by Liu et al. (2). The electrodes and electrolyte assembly is in the shape of a circular disc held between the air outlet tube on one side and the fuel outlet tube on the other. On both sides, the inlet tube is the inner one and the outlet tube, concentric with the inlet, is the outer tube. This geometry is very common and is also known as a "button cell". The inlet gases flow in along the inner tube and the exhaust flows out through the annular space between the inner and outer tubes. The data sets that are used in this work to validate the models are from a sample cell that used Co-Mo-S mixed with Ag as anode and Pt as cathode. The electrolyte was 8 mol% YSZ.

Two models of the above SOFC are discussed in this work, 1) an algebraic model derived by integrating a one dimensional model along the thickness of the cell, and 2) a two dimensional finite element axisymmetric model.

1-D Model

In developing this model we followed a similar approach to that detailed in Kim et al. (9) and Chan et al. (10). A one-dimensional analysis was done along the thickness of the cell to obtain a model equation [3] that relates the voltage, \( V \) of the working cell to the current density, \( i \) drawn from the cell.

\[
V = E_{oc} - i R_Q - \eta_{act-anode} - \eta_{act-cathode} - \eta_{conc-anode} - \eta_{conc-cathode} \quad [3]
\]

\( E_{oc} \) is the open circuit voltage, \( R_Q \) is the total ohmic resistance (cell area specific) of the cell, \( \eta_{act} \) are the activation voltage losses at the anode and cathode, and \( \eta_{conc} \) are the concentration (mass transfer) voltage losses. The activation and concentration (mass transfer) voltage losses in our model are given in the equations [4].

The ohmic resistance includes the resistance of the zirconia electrolyte, the electrodes and the contact resistance. Any current lead wire or inter-phase resistance is bundled into \( R_{contact} \). The activation losses assume a Butler-Volmer (11) kinetic expression where the exchange coefficient is 0.5. The concentration voltage loss terms have the limiting current densities \( i_{a,l} \) and \( i_{c,l} \) as parameters. \( K \) in equation [4d] is a
\[ R_Q = \rho I_{\text{RSZ}} + \rho I_{\text{anode}} + \rho I_{\text{cathode}} + R_{\text{contact}} \]  

\[ \eta_{\text{act-anode}} = \frac{2RT}{n_e F} \sinh^{-1} \left( \frac{i}{2i^o_a} \right) \]  

\[ \eta_{\text{act-cathode}} = \frac{2RT}{n_e F} \sinh^{-1} \left( \frac{i}{2i^o_c} \right) \]  

\[ \eta_{\text{conc-anode}} = -\frac{RT}{2F} \ln \left( \frac{1 - \frac{i}{i^o_a}}{1 + K \left( \frac{i}{i^o_a} \right)^{1.5}} \right) \]  

\[ \eta_{\text{conc-cathode}} = -\frac{RT}{4F} \ln \left( 1 - \frac{i}{i^o_c} \right) \]  

function of initial partial pressures of H\textsubscript{2}S, H\textsubscript{2}O, and S\textsubscript{2}. \( V_{oc} \) in the model is taken from experimental data set being modeled instead of being calculated using Nernst equation. This is done as the formal potential for the cell is not known and the open circuit voltage is probably a mixed voltage from the different possible reactions at the anode (3, 4).

One way to validate this model is to obtain all the parameters needed from published or experimental data and then match the model results against the given performance data. Another is to estimate them from given voltage-current density data and then validate against other data sets. This is the approach we propose to follow. An implementation of non-linear least squares in the Optimization Toolbox of MATLAB (12) was used to fit parameters in the model to the data and the obtained fit and parameter values are discussed in the results section. Validation against new data sets will be the next step in this study.

2-D Model

In developing the 2-D model, the cylindrical geometry of the cell and the symmetry around the central axis is used to reduce the modelling domain to a 2-D axi-symmetric domain as shown in Figure 1. The sub-domains in this reduced domain are (going left to right in Figure 1): (i) the fuel flow channel, (ii) the anode, (iii) the electrolyte, (iv) the cathode, and (v) the air flow channel.

The 2-D model built using FEMLAB (13) solves the i) Navier-Stokes equations and Brinkman’s equations for velocity and pressure in the flow channels and electrodes respectively, ii) Convection-Diffusion mass transfer equations for partial densities of H\textsubscript{2}S, H\textsubscript{2}O, S\textsubscript{2} on the fuel side and O\textsubscript{2} on the air side and, iii) Laplace equation (Ohm’s law) for the voltage/current distribution in the electrodes and electrolyte. Heat transfer is not modeled as yet.

The full details of the model are not given here for the sake of brevity. However, some salient features of this model are:
Figure 1. Modeling domain for 2-D model.

- mass transfer in electrodes takes account of Knudsen diffusion;
- electrochemical (EC) reaction takes place at the electrode-electrolyte interface only – modeled by boundary conditions;
- form of Butler-Volmer equation used to model the EC reactions includes local concentrations at the electrode-electrolyte interface [5].

\[ \tilde{i}_{\text{anode}} \bigg|_{\Omega_{\text{anode-electrolyte}}} = \tilde{i}_{\text{anode}}^0 \left( \frac{c_{H_2S}^0 \exp\left(\frac{2(1-\beta)\eta_a F}{RT}\right)}{c_{H_2S}^0} - \frac{c_{H_2O}^0 \sqrt{c_{S_2}^0} \exp\left(-2\beta\eta_a F\right)}{c_{H_2O}^0 \sqrt{c_{S_2}^0}} \right) \]  

\[ \tilde{i}_{\text{cathode}} \bigg|_{\Omega_{\text{cathode-electrolyte}}} = \tilde{i}_{\text{cathode}}^0 \left( \sqrt{\frac{c_{O_2}^0}{c_{O_2}^0}} \exp\left(-2\beta\eta_c F\right) - \exp\left(\frac{2(1-\beta)\eta_c F}{RT}\right) \right) \]  

CURVE-FITTING RESULTS AND DISCUSSION

In the model equations for the 1-D model, [3] and [4], \( r_a \) and \( r_c \), \( i_{an} \) and \( i_{cat} \), and \( R \) can be considered as parameters. These parameters were calculated using non-linear least squares for three data sets obtained from one cell at 750, 800, and 850°C (data taken from Figure 10 in Liu et al. (2)). The IR compensated versions of these data sets were also fitted using the same model by removing the ohmic loss term from [3]. There are three different ways to fit these data: i) fit the actual \( i-V \) curves by themselves, ii) fit the IR compensated \( i-V \) curves, iii) fit both simultaneously. All data sets were first smoothed and filtered to remove outliers and duplicate values.

When fitting the actual \( i-V \) curves, almost perfect fits are obtained for the data at 800 and 850°C while the fit for 750°C is not quite as good (Figure 2). Among the IR compensated data sets, only the data at 850°C can be reasonably fitted as seen in Figure 3. Similarly, Figure 4 shows that when fitting both the actual and the IR compensated data together,
the fit for data at 850°C is far better than that for 750 and 800°C. However, the trends in the fitted parameters with respect to temperature make sense, with increasing T, the total ohmic resistance drops and the exchange current densities increase (Table 1). The accuracy of the calculated limiting currents, \(i_{\text{as}}\) and \(i_{\text{cs}}\), is suspect because only the IR compensated data at 850°C seems to go to a high enough current density where concentration voltage losses are dominant. But even for this data set, calculating both \(i_{\text{as}}\) and \(i_{\text{cs}}\) separately and reliably is not possible. If the fitted value for \(i_{\text{as}}\) at 850°C is used to calculate \(D_{\text{eff}}\) and compared to \(D_{\text{H}_2\text{S-H}_2\text{O}}\) calculated using the Fuller-Schettler-Giddings equation (14), \(D_{\text{H}_2\text{S-H}_2\text{O}}/D_{\text{eff}} \sim 500\). This suggests a low porosity/tortuosity ratio and significant Knudsen diffusion effects.

![Graph](image)

**Figure 2. Model fit to actual cell performance data.**

**Table 1. Parameters fitted in 1-D model and measure of fit.**

| Data used to build model | \(T^\circ\text{C}\) | \(i_{\text{as}}\) A/m² | \(i_{\text{cs}}\) A/m² | \(i_{\text{el}}\) A/m² | \(i_{\text{c,l}}\) A/m² | \(R_D\) Ω | \(\Sigma (V-V^2)\) |
|-------------------------|----------------------|---------------------|---------------------|---------------------|---------------------|----------|---------------------|
| Actual data             | 750                  | 5060                | 32.5                | 1.64e5              | 3000                | 7.31e-4  | 0.0197              |
|                         | 800                  | 229                 | 229                 | 7110                | 8.79e4              | 4.76e-4  | 0.00138             |
|                         | 850                  | 388                 | 388                 | 6000                | 6.78e4              | 3.65e-4  | 0.00107             |
| IR-comp. data           | 750                  | 32.2                | 32.2                | 3000*               | 3000*               | -        | 2.7                 |
|                         | 800                  | 104                 | 104                 | 4000*               | 4000*               | -        | 1.50                |
|                         | 850                  | 286                 | 286                 | 4510                | 4510                | -        | 0.387               |
| Both                    | 750                  | 37.4                | 37.4                | 3000*               | 3000*               | 3.67e-4  | 3.96                |
|                         | 800                  | 112                 | 112                 | 4000*               | 4000*               | 3.39e-4  | 1.99                |
|                         | 850                  | 290                 | 290                 | 4510                | 4510                | 3.17e-4  | 0.438               |

* Values with asterisks are at the bounds specified in the optimization routine.
The overall ohmic resistance calculated for this cell is very high (Table 1). The electrolyte’s area specific resistance at 800°C is \( R = \rho l = 0.33 \times 2 \times 10^{-5} = 6.6 \times 10^{-5} \ \Omega \text{m} \)
whereas the cell's overall ohmic resistance is several times higher at $3.8 \times 10^{-4}$ Ωm (3.8 Ω as cell area is 1 cm$^2$). The cell's overall ohmic resistance is a sum of the resistances of the electrodes, the electrolyte, contact resistances at the current collectors, resistance of the current leads to the cell and any other resistive phases in the cell layers. The electrode resistivities are much lower than that of YSZ, the cathode is platinum while $\rho_{\text{anode}} = 0.04$ Ωm (2). This suggests that the difference between overall cell and electrolyte resistance must be from a combination of contact resistances, lead wires and resistive phases in the cell layers.

The 2-D model can be made to fit data fairly well (Figure 5) just by searching for exchange current density values that generate $i-V$ curves matching the data. However, the $i^c$ values in the 2-D model that fit the data are significantly higher than those estimated for the 1-D model. One possible reason for this is large differences in the concentration voltage losses between the two models, those in 2-D model being lower ($D_{\text{H}_2\text{S-H}_2\text{O}}/D_{\text{eff}} \sim 50$). Another reason could be the inclusion of local concentrations in the Butler-Volmer type kinetic expressions (equation [5]) used in the 2-D model.

![Figure 5. 2-D model output.](image)

**CONCLUSIONS**

A SOFC fuelled with H$_2$S is modeled using both a simple 1-D model as well as a more complex 2-D model. Important physical and kinetic parameters in the 1-D model are fitted using experimental data sets at three different temperatures and reasonable fits are obtained for the data sets at 800°C and 850°C. However, the third data set at 750°C does not give a good fit using this model. We need to apply the curve-fitting to more data sets to investigate it further. Other data that would be very useful are kinetic data that give exchange current densities, or even better, reaction mechanisms and rate constants, at the two electrodes. The main conclusion that can be drawn from the present study is that the ohmic resistance of the cell is very high. Contact resistances are believed to be the reason...
behind this although there could be contributions from resistive interphases. The laboratory research group is working on improving current contacts in the cell.

The 2-D model also gives reasonable fits only to the higher temperature data sets. The reasons for this are unknown at this point. One of the things we want to try next is to fit the exchange current densities in the 2-D model using non-linear least squares in a similar manner to the 1-D model. Wei et al. (4) presented very interesting data that shows the cell performance being a strong function of fuel flow-rate. We want to try and model this behaviour and will have to depend on the 2-D model as the 1-D model does not have flow-rates as parameters.

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