THE SIMULATION OF SOLID OXIDE FUEL CELL MEMBRANE-ELECTRODE ASSEMBLY

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ABSTRACT

A solid oxide fuel cell (SOFC) Membrane Electrode Assembly (MEA) simulation model and the corresponding FORTRAN coding strategy are presented. For a given fuel/oxidant composition and MEA configuration, this newly developed code can predict the cell output voltage and polarizations versus the cell current density. The activation polarization is evaluated by solving the Butler-Volmer equation. The concentration polarization is based on the dusty-gas model. The ohmic polarization is obtained by considering the ionic conductivity of the electrolyte. Leakage polarization is also included in the model. The FORTRAN code, written as a stand alone module, has been used to predict the performance of SOFCs. This code could be easily incorporated into a computational fluid dynamics code as a SOFC sub-module for three dimensional fuel cell simulations.

INTRODUCTION

Fuel cells are electrochemical devices, which utilize fuel and oxidant to produce electricity and heat (1). Because the fuel is converted chemically to electricity, fuel cells operate at higher efficiencies than conventional internal combustion engines or gas turbines. Fuel cells are classified by the electrolytes. The basic physical structure of a single fuel-cell consists of an electrolyte layer in contact with a porous anode and cathode on either side. The electrochemical reactions take place at the electrode-electrolyte interfaces. The most common electrolyte of a SOFC for high temperature applications is yttria-stabilized zirconia (YSZ) (2,3). YSZ conducts oxygen ions because of oxygen vacancies created in the crystal lattice by the doping of yttrium oxide. SOFC usually operates at a temperature between 800°C and 1000°C. The high operating temperature provides the necessary thermal energy to overcome the activation energy and to increase the ionic conductivity of the electrolyte. Because of the high operation temperature, the need for expensive catalysts is eliminated and the bottoming gas/steam turbines could be integrated with SOFC systems for further improvement of system efficiency (4,5).

In this work, a SOFC Membrane-Electrode Assembly (MEA) simulation tool is developed. Figure 1 shows the schematic diagram of a SOFC membrane-electrode assembly (MEA), which has a sandwiched anode-electrolyte-cathode structure.
A SOFC system involves complex species transport, chemical reactions, thermal and electrochemical processes. Transport resistances of the gaseous species in the feed channels and the porous electrodes lead to the so-called concentration overpotential; the transportation of $O_2^-$ in the electrolyte layer forms a large portion of total ohmic loss; the activation energy barriers for the electrochemical reactions are related to the charge-transfer processes at the electrode-electrolyte interface. Due to these losses (6,7,8,9,10), the voltage of a single cell is much less than its theoretical value. These losses are functions of both operating conditions and the physical properties of the cell. The operating conditions include temperature, pressure, and fuel and oxidizer concentrations. The MEA properties include the macro- and micro- structures of the electrodes and the electrolyte; the ionic conductivity and the thickness of the electrolyte, the active area and activity of the electrode-electrolyte interface. In this work, a computational code based on a unit-cell MEA physical model, considering various overpotentials, has been developed to simulate the performance of SOFC MEAs.

**MODEL FORMULATIONS**

The output voltage of a fuel cell can be expressed by corresponding Nernst potential and polarizations, Eq. 1:

$$E_{cell} = E - \eta_{conc,a} - \eta_{act,a} - \eta_{ohm} - \eta_{conc,c} - \eta_{act,c} - \eta_{leakage}$$

The definition of the terms can be found in Nomenclature. The Nernst potential, $E$, is a function of the ideal electrochemical reaction and the operating conditions. The relationship between the output voltage and the cell current density is the most important fuel cell characterisation curve. Usually all polarizations are affected by the cell current density.

**Global Electrochemical Reaction**

The global electrochemical reaction can be written as:

$$\sum_{i=1}^{K} v_i x_k \longleftrightarrow \sum_{i=1}^{K} v_i x_i$$

By separating the reactants and products species, the reaction equation can be written in the form of Eq. 3:
Before the cell potential could be evaluated, Eq. 3 must be balanced to determine the reaction coefficients. Because of the linearity of this equation, arbitrarily $v_f' = 1$ can be set. Although some inert species do appear in the fuel/oxidizer streams, the reaction coefficients for such gases are set to be zeros. The total number of electrons, $n_e$, transferred by the global electrochemical reaction for each fuel atom can be determined by counting the effective oxygen-ions transferred through the electrolyte.

**Nernst Potential and the Nernst Equation**

The Nernst potential of a reaction can be expressed as

$$E = E^0 + \frac{RT}{n_e F} \sum_{k=1}^{K} (v_k' - v_k^0) \ln \left( \frac{p_k}{p_T} \right)$$  \[4\]

where the idea Nernst potential of the reaction $E^0 = -\frac{\Delta G^0}{n_e F}$, $p_k$ is the partial pressure of the $k$th species, and $p_T$ is the total pressure in the channel. The Nernst potential could be represented using the species concentrations:

$$E = E^0 + \frac{RT}{n_e F} \sum_{k=1}^{K} (v_k' - v_k^0) \ln [X_k] + \frac{RT}{n_e F} \ln \left( \frac{RT}{p_0} \right) \sum_{k=1}^{K} (v_k' - v_k^0)$$  \[5\]

**Concentration Polarization**

The concentration polarization is caused by the diffusive resistance in the electrodes. It is determined mainly by the difference of species concentrations in the mainstream and the reaction sides

$$\eta_{conc} = \frac{RT}{n_e F} \sum_{k=1}^{K} (v_k' - v_k^0) \ln \left( \frac{[X_k]}{[X_k]^*} \right)$$  \[6\]

or

$$\eta_{conc.a} = \frac{RT}{n_e F} \sum_{k=1}^{K} (v_f' n_{f,k} - v_f^0 n_{f,k}) \ln \left( \frac{[X_k]}{[X_k]^*} \right)$$  

$$\eta_{conc.c} = \frac{RT}{n_e F} \sum_{k=1}^{K} (v_o' n_{o,k} - v_o^0 n_{o,k}) \ln \left( \frac{[X_k]}{[X_k]^*} \right)$$  \[7\]

To evaluate the concentration overpotential for a MEA, the dusty-gas model (10,11,12,13) can be used. It provides the relationship between the species concentrations in the fuel/oxidizer channel and the concentrations at the electrochemical reaction sites. The Dusty Gas Model (DGM) can be written as (10):
In equations (8) and (9),

\[ \phi_g = \frac{\phi_g}{T_g} \]
\[ K_g = \frac{K_g}{T_g} \]
\[ B_g = \frac{\phi_g d^2}{72 \tau_g (1 - \phi_g)^2} \]
\[ D_{g,k} = \phi_g D_{g,t} \]
\[ D_{g,k} = \frac{4}{3} \frac{K_g}{W_k} \sqrt{\frac{8RT}{\pi W_k}} \]
\[ N_{g,a} = -\left( v_{f,n_{g,k}} - v_{r,n_{g,k}} \right) \frac{i_e}{n_{f}} \]
\[ N_{g,c} = \left( v_{f,n_{g,k}} - v_{r,n_{g,k}} \right) \frac{i_e}{n_{f}} \]

For inert gas species, \( N_{g}^{g} = 0 \).

In this model, regardless of whether the dusty-gas model is applied to the anode or the cathode, the concentrations of the species used in Eqs. 8 and 9 must be the concentrations on the upstream side of the total flux over all the species; in other words, \( \sum_{k=1}^{K} N_{g}^{g} > 0 \) the concentrations used for anode are those on the reaction site; for the cathode side, they are those in the flow channel, and vice versa. Most commonly, for the SOFCs with an oxygen-ion conductor electrolyte the total species flux is towards the positive flux direction; and for the SOFCs with a proton conductor electrolyte, the total flux direction is usually towards the negative flux direction.

The species concentrations on the reaction sites that are needed in Eqs 8 and 9, have to be solved by iterations. Applying the DGM on an electrode whose concentrations are unknown, based on the species concentrations in the corresponding channels, the initial guesses can be assigned. Then using Eq (8), the pressure gradient can be obtained. Substituting this pressure gradient into Eq (9), a set of new concentration gradients can be calculated. With these new concentration gradients and the concentrations in the centre of flow channels, next iteration of concentrations on the electrode reaction sites can be found. By assuming that the profiles of the species concentrations across an electrode are linear, which has proved to be valid by experiments over a large range of operating conditions and electrode structures, the analysis could be greatly simplified. The iteration converges rapidly; for most cases, only two or three iterations are needed.
**Activation Polarization**

The chemical reaction barriers cause the so called activation polarization. It can be calculated by solving the Butler-Volmer equation iteratively

\[
\eta_{act} = \frac{RT}{\alpha_e n_e^{\text{F}}} \ln \left[ \frac{i}{i_0} + \exp \left( -\frac{\alpha_e n_e^{\text{F}} \eta_{act}}{RT} \right) \right]
\]  

[10]

With an initial guess of \( \eta_{act} = 0 \), iteration can be used to find the final solution.

**Ohmic Polarization**

This loss is due to the electric resistance of the electrodes and the ionic resistance of the electrolyte. Since the electric resistance of the electrode is usually small, only the ohmic polarization due to the ion conductive electrolyte is considered in the code. The electric current flow in the MEA obeys Ohm’s law, which can be expressed as

\[
\eta_{\text{ohm}} = i R_{\text{tot}}
\]  

[11]

where

\[
R_{\text{tot}} = R_{\text{el}} + R_{\text{ed}} \approx R_{\text{el}}
\]

**Leakage Polarization**

Because the electrolyte materials are not perfect electrical insulators, there is a small electric current flow though the electrolyte. In the code, the leakage overpotential is modelled using equation 12:

\[
\eta_{\text{leakage}} = \eta_{\text{leakage}}^0 \left( 1 - \frac{i}{i_{\text{max}}} \right)
\]  

[12]

\( \eta_{\text{leakage}}^0 \) can be obtained experimentally for a particular type of electrolyte. \( i_{\text{max}} \) can be determined from the model by calculating the current when the output voltage vanishes.

**PROGRAMMING**

**The Basic Calculation Algorithm**

The code determines the SOFC output voltage for a given current density. Since the overpotentials are usually implicit functions of current densities, iterations are necessary. The coding algorithm can be summarised in the following steps:

1. Obtain correct reaction coefficients for the reaction equation 3.
2. Evaluate the species concentration in the channels \([X_i]\) under the operating temperatures and pressures.
3. Based on equation 3, calculate the charge $n_e$, and the Nernst potential $E$ (Eq. (4) or (5)).
4. Assume a current density $i_e$
5. Evaluate the species molar fluxes through the electrodes $N_f$
6. Apply the dusty-gas model (Eq. (8) and (9)) on both anode and cathode respectively to calculate the species compositions at electrode-electrolyte interface $[X_k]^f$. Iteration is needed.
7. Evaluate the concentration overpotentials for both electrodes $\eta_{\text{conc},a}$ and $\eta_{\text{conc},c}$ (Eq. (7)).
8. Calculate the activation polarizations for both electrodes $\eta_{\text{act},a}$ and $\eta_{\text{act},c}$, using the Butler-Volmer equation, Eq. (10). This is an iterative procedure.
9. Determine the ohmic overpotential $\eta_{\text{ohm}}$ (Eq. (11)).
10. Calculate the leakage polarization $\eta_{\text{leakage}}$ (Eq. (12)). Since the maximum current density $i_{\text{max}}$ is unknown at this stage, it is an iterative process. After $i_{\text{max}}$ is obtained, for a given current density $i_e$, $\eta_{\text{leakage}}$ can be determined.
11. Finally the cell output voltage $E_{\text{cell}}$ (Eq. (1)) can be evaluated for a given current density.

This procedure can be repeated for a range of current densities, thus a current-voltage plot can be obtained.

**The Flow Chart**

The flow chart of the code is shown in Fig. 2. The parameters about the reactions, the operating conditions and the MEA structures should be supplied as inputs to the code first. These input data will then be converted into variables which can be directly used by the dusty-gas model. After the first iteration, including the evaluation of the reaction Nernst potential under the operating conditions, the maximum current density for the cell could be found. The leakage polarization is to be ignored in this step. As the leakage polarization varies linearly with the current density and at the maximum current density is zero, thus it will not affect the predicted maximum current density. After finding the maximum current density, the second iteration is performed by stepping through the current density range. At each current density step, all overpotentials including the leakage overpotential and the cell output voltage will be evaluated and saved in a prescribed file.

**Figure 2. Flow chart.**
The working process of the first iteration is shown in Fig. 3. For different exit conditions, different interpolations are used to obtain the maximum current. For cases involving negative species concentrations in the calculation, the ‘imax (1)’ and ‘imax (2)’ in the flow chart, the values of the negative concentration species at the last two current density iterations will be used to determine the maximum current density. For the case where the output voltage reaches zero first, the ‘imax (3)’, the last two values of voltage will be used for extrapolation. Figure 4 illustrates methods of finding the maximum value of current density. The second iteration has a similar structure, shown in Fig. 5, except that the maximum current density is already known so that the leakage overpotential can be evaluated at each current density step. Figure 6 shows the flow chart of the process of solving the dusty-gas model.

![Flow Chart for the First Iteration](image)
Figure 4. The scheme to choose the maximum current density. Right: The output voltage vanishes first before species concentrations at TPB reach zero; Left: The species concentrations at TPB reach zero before output voltage reaches zero.

Figure 5. Flow Chart for the Second Iteration.
RESULTS AND DISCUSSION

This newly developed code has been applied to an anode-supported SOFC MEA structure with hydrogen as fuel. The cell configurations are listed in table 1 and the working temperature is 1023K and pressure is 1 atm. Figure 7 shows the cell output voltage, output power density and all the polarizations as a function of current density.

As the current density increases, the cell output voltage decreases from the Nernst potential to zero at the maximum value of current density. In other words, as the current density is rising, the level of the polarizations increases; at the maximum current density, all the Nernst potential contributes to the polarizations. As the current density increases, the output power density initially goes up; around the current density of half the maximum value, it develops a peak; and then the power density drops with the output voltage. The leakage and ohmic overpotentials are distributed linearly. The leakage polarization intercepts the 'Voltage' axis at its maximum and becomes zero at the maximum current. The ohmic overpotential increases linearly from zero. The calculated anode and cathode activation polarizations curves are shown in Figure 8. The cathode activation polarization is obviously higher than that of the anode due to its lower exchange current density. Figure 9 shows the profiles of the anode and cathode concentration polarizations. Since the code is applied to an anode-supported MEA structure, the anode concentration polarization is much higher than that of the cathode.
Table 1: MEA configuration used in calculation.

| Parameter            | Value   |
|----------------------|---------|
| **Anode**            |         |
| Thickness (µm)       | 1000    |
| Porosity             | 0.35    |
| Tortuosity           | 3.5     |
| Average Pore Radius (µm) | 1   |
| Average Particle Diameter (µm) | 10 |
| Exchange Current Density (A/cm²) | 0.40 |
| Charge-Transfer Coefficient | 0.50 |
| Number of Electrons  | 1       |
| **Cathode**          |         |
| Thickness (µm)       | 50      |
| Porosity             | 0.35    |
| Tortuosity           | 3.5     |
| Average Pore Radius (µm) | 1   |
| Average Particle Diameter (µm) | 10 |
| Exchange Current Density (A/cm²) | 0.13 |
| Charge-Transfer Coefficient | 0.50 |
| Number of Electrons  | 1       |
| **Electrolyte**      |         |
| Thickness (µm)       | 20      |
| Activation Energy of O²⁺ (J/mol) | 8e+4 |
| Pre-Factor of O²⁻ (S/cm) | 3.6e+5 |
| Leakage Overpotential (V) | 0.07 |

Figure 7. Cell Voltage, Power Density and Polarizations versus the Current Density for a H₂ SOFC.
CONCLUSIONS

A new mathematical code has been represented, which simulates the performance of a solid oxide fuel-cell membrane-electrode assembly under specified operating conditions. By considering the variation of activation, concentration, ohmic and leakage polarizations, this code can produce a voltage-current relationship for prescribed MEA configurations. The MEA could be anode-supported, electrolyte-supported or cathode-supported. The code gives well behaved and expected data trend. By running this code, the SOFC I-E curve can be easily obtained. The precision of the model, especially the dusty-gas model section could be further improved by validating the code against the experimental data. The code is compact and converges rapidly. Although it acts as a stand alone SOFC prediction tool at the moment, it could be easily embedded into a large Computational Fluid Dynamics based SOFC simulation system.

NOMENCLATURE

| Symbol | Description |
|--------|-------------|
| $E$ (V) | Nernst potential |
| $v'$ | Reaction coefficient for reactants |
| $v^*$ | Reaction coefficient for products |
| $\chi$ | Chemical symbol |
| $\eta$ (V) | Polarization |
| $i_e$ (A) | Current density |
| $n$ | Composition Fraction |
| $N^e$ (mol/s) | Species molar flux |
| $D_{id}$ (m²/s) | Binary diffusion coefficient |
| $D_{id}^{*}$ (m²/s) | Effective binary diffusion coefficient |
| $D_{ks}^{e}$ (m²/(J/kg)^{1/2}) | Effective Knudsen diffusion coefficient |
| $i_0$ (A) | Exchange current density |
| $R_{mr}$ (Ω) | Total resistance |
| $R_d$ (Ω) | Resistance of the electrolyte |
| Symbol | Description |
|--------|-------------|
| $R$ (8.314 J/(mol·K)) | Universal gas constant |
| $p$ (Pa) | Pressure |
| $T$ (K) | Temperature |
| $F$ (96485 C/mol) | Faraday's constant |
| $n_e$ | Electron number |
| $[X]$ (mol/m$^3$) | Species concentration |
| $[X]_e$ (mol/m$^3$) | Equilibrium species concentration |
| $[X]^c$ (mol/m$^3$) | Species concentration in channel |
| $[X]^a$ (mol/m$^3$) | Species concentration at TPB |
| $\Delta G^0$ (J/mol) | Standard Gibbs function |
| $\mu$ (N·s/m$^2$) | Viscosity |
| $\rho_f$ | Porosity-to-tortuosity ratio |
| $\phi_f$ | Porosity |
| $\tau_f$ | Tortuosity |
| $K_f$ (m) | Knudsen coefficient |
| $r_p$ (m) | Average pore radius |
| $d_p$ (m) | Average particle diameter |
| $B_s$ (m$^2$) | Permeability constant |

| Symbol | Description |
|--------|-------------|
| $R_{cd}$ (Ω) | Resistance of the electrode |
| $\sigma$ | Electrolyte ionic conductivity |

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