A COMBINED NUMERICAL AND EXPERIMENTAL INVESTIGATION FOR THE DEVELOPMENT OF UNDERSEA SOLID OXIDE FUEL CELL SYSTEMS

Eric S. Greene1, Wilson K. S. Chiu1, Maria G. Medeiros2
A. Alan Burke2, and Louis G. Carreiro2

1University of Connecticut, Department of Mechanical Engineering
191 Auditorium Rd., Storrs, CT 06269, USA
2Naval Undersea Warfare Center, Code 8231, 1176 Howell St., Newport, RI 02841, USA

ABSTRACT

Solid oxide fuel cells (SOFCs) have been identified as a potential power source for future unmanned undersea vehicles. They offer efficient and stealthy operation. A research and development program has been designed to identify and address the issues in SOFCs specific to operation in the undersea environment. The main component of this is a linked experimental and modeling study. A validation of the model presented for pure hydrogen and oxygen reactant streams showed agreement with a maximum of 1% difference. The model will be used to optimize SOFC systems for undersea operation.

INTRODUCTION

A solid oxide fuel cell (SOFC) system has been identified as a potential power source in the 1-5 kW power range for future unmanned undersea vehicles. The combination of efficiency, stealth operation, balance of plant (BOP) simplicity, high system energy density, and fuel flexibility lead to the selection of SOFCs as the future technology for this application. Design and implementation of a research and development program to address the issues in SOFCs, concentrating on the areas specific to operation in the undersea environment, are described in this paper.

Operation in an undersea environment imposes constraints that are significantly different or not addressed by land-based SOFC development programs. These include air independent oxidant source, stack temperature regulation, startup times, acceptable lifetime, and system energy density. The potential for using a pure oxygen source and the benefits to total system energy density gained by using hydrocarbon fuels are two of the most important effects of these issues.

The approach used to address the issue of undersea operation and results obtained to date are described in this paper. The approach taken couples the use of experiments and numerical modeling studies to identify areas for improvement in the underwater SOFC system. The experiments both validate the model, help to identify important physics of the system, and suggest areas to be addressed with modeling. The results are then used to improve the modeling capabilities, investigate alternative system designs, and assist in the design of higher performance fuel cells to be tested in the experimental setup. The use
of a combined and flexibly-designed experimental and numerical approach will be an advantage in developing SOFCs for undersea operation.

APPROACH

Experimental Method

SOFC button cells one inch in diameter (active area) were obtained from two commercial vendors, Ceramatec and InDEC. Ceramatec's electrolyte-supported cells, supplied test-ready with platinum electrical contacts attached, were evaluated for their electrochemical performance. InDEC's anode-supported cells, received as wafers, were examined for microstructure and elemental composition. Note that small cell size aids in investigating the general effectiveness of various material systems, as well as in designing a fixture that is able to provide precise gas flow to the electrode surfaces. The latter results in maintaining gas concentrations that are effectively constant across the cell surface, hence creating a one-dimensional system.

The experimental setup is designed to be modular so that components can be upgraded as the size of the test cell is increased. The design schematic is shown in Figure 1 and includes a clamshell furnace surrounding a concentric tube fixture in which gas and oxidant are supplied on opposite sides of a cell cemented to the ends of the tubes. The inner tube creates an impinging jet of reactant that can simulate constant surface conditions when the flow is raised so that the change in concentration across the surface is negligible.

Figure 1. Diagram of the solid oxide fuel cell testing stand.

Scanning electron microscopy (SEM) with electron dispersive spectroscopy (EDS) was used to examine the microstructure and chemical composition of the InDEC anode-supported cells. This is undertaken both before and after running the cell. Porosity, pore sizes, and electrode and electrolyte thicknesses were estimated from the micrographs.
**Numerical Method**

Modeling of the SOFC is achieved using a one-dimensional geometry. This is appropriate for matching with the experiments that were performed. The modeling domain is diagrammed in Figure 2. The model calculates the cell overpotential from several physical sources (1) and determines the cell potential at a given current density.

![Model Domain Diagram](image)

**Figure 2. Numerical model domain of the solid oxide fuel cell.**

The expression for the operating voltage of the cell is calculated according to:

$$E_{op} = E - \eta_{act} - \eta_{ohm} - \eta_{conc} \quad [1]$$

In Eq. 1, $E_{op}$ is the operational fuel cell voltage, $E$ is the ideal Nernst voltage calculated from thermodynamic principles, $\eta_{ohm}$ is the overpotential caused by electronic and ionic ohmic losses from current flowing through the fuel cell materials, and $\eta_{conc}$ is the voltage loss caused by reduced fuel and oxidant concentrations. These are all highly dependent on current density.

The Nernst voltage can be calculated for a H$_2$/O$_2$ fuel cell by:

$$E = E^o + \frac{RT}{2F} \ln \frac{p_{H_2}p_{O_2}^{0.5}}{p_{H_2O}} \quad [2]$$

$R$ is the universal gas constant, $p_i$ is partial pressure for species $i$, and $F$ is Faraday's constant. The thermodynamically maximum voltage obtainable for a given temperature ($E^o$) is calculated according to Eq. 3, which utilizes the Gibbs free energy difference ($\Delta G^o$) between fuel cell products and reactants, where $n$ is the number of equivalent electrons per mole reacted.

$$E^o = -\frac{\Delta G^o}{2F} \quad [3]$$

The activation overpotential can be accurately modeled by the Butler-Volmer equation for a fuel cell (2):
This equation includes the exchange current density \( i_0 \) and the transfer coefficient \( \beta \).

The ohmic losses through the cell components, \( \eta_{\text{ohm}} \), are found by using Ohm’s law. The voltage drop is proportional to the current by \( \eta_{\text{ohm}} = iR \) where the resistance, \( R \), is the product of the materials resistivity, \( \rho \), and the thickness of the layer, \( L \). The total ohmic loss is then the sum of the three component losses from the anode, cathode, and electrolyte.

The concentration polarization occurs due to reduced reactant concentrations at the electrochemically active regions. Many situations can lead to significant resistance to mass transfer through the porous electrodes. This causes a concentration gradient of products and reactants across the electrode that leads to lower concentrations of reactants at the triple phase boundary where reactants are used. The concentration polarization, \( \eta_{\text{conc}} \), is the difference in Nernst potential, calculated using calculated gas compositions, between the reactant supply channel, \( E^{\text{sup}} \), and the triple phase boundary, \( E^{\text{TPB}} \) (3).

\[
\eta_{\text{conc}} = E^{\text{sup}} - E^{\text{TPB}}
\]

Modeling mass transport in the electrodes is essential to obtaining the necessary concentrations for calculating the concentration polarization. The mean transport pore model (MTPM) (4,5) is used to approximate the geometry of a porous media as continuous round pores from the electrode surface to the interface with the electrolyte. Within the framework of the MTPM, the electrode geometry is described by three parameters:

- \( \Psi \) - the ratio of porosity over tortuosity of the relevant gas transport pores
- \( \langle r \rangle \) - the mean value of pore radii
- \( \langle r^2 \rangle \) - the mean value of the transport pore radius squared

The parameter \( \Psi \) can be thought of as a measure of the effective porosity of the material. It adjusts the real porosity for the extra resistance that the tortuous path imposes to the flow of gasses. Knudsen diffusion must be taken into account in the calculations because the pore sizes are on the same order of magnitude as the mean free path length of the gasses. The total mass transport is given by:

\[
N_i = N_i^d + N_i^p
\]

Where \( N_i^d \) is the total component diffusion flux and \( N_i^p \) is the total component permeation flux. Stefan-Maxwell diffusion is modified to represent Knudsen diffusion:

\[
\frac{N_i^d}{D_i^k} + \sum_{j=1}^{n} \gamma_{ij} \frac{N_i^d - N_j^d}{D_j^m} = -c_y \frac{dy_i}{dx}.
\]
Total component flux can be described by the modified Darcy equation:

\[ N_i^p = -y_i B_i \frac{dC_i^p}{dx} \quad i=1,\ldots,n \]  

\[ B_i = K_i \Psi(r) + \omega K_i \Psi(r)(1 - \phi) + \frac{r^2}{8\eta} \Psi P \quad i=1,\ldots,n \]

\[ \phi^{-1} = 1 + \left( \frac{\lambda}{2r} \right)^{-1} \]

In the above equations, \( K_i \) is the Knudsen number of component \( i \), \( \omega \) is a physical factor that depends on the Knudsen wall slip, and \( \nu_i \) is the square root of the relative molecular weights. Values for gases used in this study are available in the literature (6).

For boundary conditions, the composition of the fuel gas is known at the interface between the channel and the electrode interface. At the interface between the channel and electrodes, the molar flux rates of all gases are known. The resulting system of ordinary differential equations is solved using an iterative Newton-Raphson technique.

**RESULTS AND DISCUSSION**

A comparison between the experimental results of an electrolyte-supported cell and the numerical model is shown in Figure 3. There is a maximum 1% difference between the two data sets. This is within the experimental measurement error and therefore validation is shown for the model presented under the specified conditions. The maximum power density recorded was 0.178 W/cm², which is typical for electrolyte-supported cells operating under the conditions given in Table I (7). The concentration polarization for this electrolyte-supported cell is negligible. The power density requirements of the intended application of this technology require that an anode-supported cell with a thin electrolyte be used. This issue will be addressed in future experiments. The model is designed to simulate the added complexity of this electrode morphology.

**Table I. List of parameters used in validation study.**

| Parameter                  | Value   | Parameter                  | Value   |
|----------------------------|---------|----------------------------|---------|
| Temperature (T, K)         | 1273    | Cathode Thickness (Lc, µm) | 20      |
| Pressure (P, atm)          | 1.00    | Cathode Resistivity (ρ, Ωm) | 3.5     |
| Exchange Current Density (I0, A/cm²) | 0.05 | Cathode Porosity (sc) | 0.35    |
| Transfer Coefficient (β)  | 0.5     | Cathode Tortuosity (τc) | 3.00    |
| Anode Thickness (LA, µm)  | 20      | Cathode Pore Radius (r>, µm) | 0.75    |
| Anode Resistivity (ρ, Ωm) | 0.001   |                             |         |
| Anode Porosity (sa)       | 0.45    | Electrolyte Thickness (LE, µm) | 200    |
| Anode Tortuosity (τa)     | 3.00    | Electrolyte Resistivity (pe, Ωm) | 0.20 |
| Anode Pore Radius (r, µm) | 1.05    |                             |         |
Current Density (A/cm²)

Figure 3. Experimental polarization and power density comparison with the numerical model. Symbols represent experiments and curves represent model predictions.

The air-independent operation characteristics of undersea fuel cells require detailed performance considerations when a pure O₂ source is used. Model predictions for the change caused by the use of O₂ vs. air are shown in Figure 5. The parameters used are the same as shown in Table I, except the anode thickness is 600 μm, the cathode thickness is 100 μm, and the electrolyte thickness is 5 μm. These are the values measured in Figure 3 and are representative of modern high performance fuel cells. When using pure O₂, a maximum voltage increase of 6.6% and an increase of 12.3% to the maximum power are observed. Changes in the fuel cell performance can be attributed to the Nernst potential and electrode activity. The thin layers that compose most cathodes were observed to cause minimal mass transfer resistance. In the thick anode-supported cell the mass transfer was observed to be significant when fuel mixtures were used.

Figure 4. Comparison of predicted SOFC performance for pure O₂ and air as the oxidant.
Figure 5. SEM micrograph of a (a) cross-section of an anode-supported SOFC, (b) electrolyte interface, (c) anode microstructure, and (d) cathode microstructure.

SEM micrographs taken of a typical cell (InDEC) with an anode-supported structure are shown in Figure 5(a-d). Using the scale bars as a reference, the thickness of the anode is estimated to be 600 μm and the cathode 100 μm thick. In Figure 5(b) the electrode’s porous structure becomes evident. The thickness of the electrolyte can also be estimated to be 5 μm from this image. Figures 5(c) and 5(d) taken of the cell surface (not a fractured surface) show close-up micrographs of the anode and cathode. The porosity and pore radius were estimated and used for the cell modeled in Figure 4.

CONCLUSIONS

This study presents an investigation of design tools for use in undersea SOFC systems. The experimental setup and design of a fixture for full reactant control for a 1” diameter cell is shown. Results using a commercially available cell are presented and comparisons to the numerical results are shown. For the case presented, the model agrees well with experimental data. The model was also used to predict the change in fuel cell performance when O₂ is used as an oxidant as opposed to air. Future studies will include the effects of internal reforming of hydrocarbon fuels, multi-dimensional modeling, and integration of knowledge into system level models that will lead to the final goal of a SOFC system optimized for operation in an air independent undersea environment.
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NOMENCLATURE

$B_i$ = Effective permeability coefficient of species $i$ (m$^2$/s)
$c_i$ = Concentration of species $i$ (mol/m$^3$)
$c_t$ = Total concentration of species (mol/m$^3$)
$D^k$ = Gas diffusion constant (m$^2$/s)
d = thickness ($\mu$m)
$E$ = Fuel cell electrochemical potential (V)
$E^\circ$ = Theoretical maximum fuel cell electrochemical potential (V)
$F$ = Faraday's constant, 96,485 (C)
i = Current Density (A/cm$^2$)
i$_0$ = Exchange current density (A/cm$^2$)
$K$ = Knudsen number (= $\lambda/2r$)
$L$ = Thickness of layer ($\mu$m)
$N_i$ = Molar flux rate of species $i$ (mol/m$^2$ s)
p = Pressure (Pa)
p$_i$ = Partial pressure of gas $i$
$R$ = Universal gas constant, 8.314 (J/K-mol)
$<r>$ = Mean pore diameter ($\mu$m)
$<r^2>$ = Statistical distribution parameter of pore size around mean ($\mu$m$^2$)
$T$ = Temperature (K)
$y_i$ = Concentration percentage of component $i$

Greek letters

$\eta$ = Gas mixture viscosity (m$^2$/s)
$\eta_{act}$ = Activation Polarization (V)
$\eta_{conc}$ = Concentration Polarization (V)
$\eta_{ohm}$ = Ohmic Polarization (V)
\[ \lambda = \text{Mean free path length (m)} \]
\[ \Psi = \text{Ratio of porosity to tortuosity (e/\tau)} \]

*Superscripts*
- \(d\) = Diffusion
- \(k\) = Knudsen
- \(m\) = Molecular
- \(op\) = Operational
- \(sup\) = Supply
- \(TPB\) = Triple Phase Boundary
- \(p\) = Permeation

*Subscripts*
- \(A\) = Anode
- \(C\) = Cathode
- \(E\) = Electrolyte
- \(i,j\) = Component Identifier

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