

GCEP award #51922:

A Novel Solid Oxide Flow Battery Utilizing H-C-O Chemistry

Investigators

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Abstract

This project centers on a novel device that stores energy electrochemically in tanks like a flow battery, while the materials and chemistry are more akin to those of a solid-oxide fuel cell – hence the name “Solid Oxide Flow Battery” (SOFB). The SOFB is well suited for grid-scale energy storage because the energy storage capacity can be increased by increasing tank storage capacity. The objective of the project is to carry out the fundamental studies of the materials, cells, stacks, and system designs needed to validate the device concept and provide the information needed for further development. One set of challenges for SOFB technology includes the development of cells that yield the desired performance at the desired operating temperature and pressure, and that can work without significant degradation over thousands of electrolysis/fuelcell cycles. Other challenges are to develop viable stack and system designs that can yield the predicted ideal round-trip efficiencies of ~ 80%.

In the second year of this project, good progress has been made on a number of fronts ranging from electrochemical cell fabrication, to setup/operation of the pressure testing vessel, to system-level simulations. One highlight has been the development of SOFBs with a new materials set that yields an unprecedented low resistance at temperatures well below 600°C, as required for an efficient SOFB. Results on cyclic testing of air electrodes shows that stability is improved by frequently reversing the current direction, whereas degradation is eliminated for current density of 0.5 A/cm². The new pressurized testing setup is complete and preliminary cell tests have been successful. The past year’s modeling efforts have included fundamental thermodynamics of reversible cells at the button and cell-levels and dynamic cell-level model development, which will be employed as a design and simulation tool for stack and system studies. The research has also focused on developing a high-fidelity, dynamic SOC stack simulation tool, input needed for making accurate system level model predictions. There has been a continued focus on analyzing system concepts and gas storage and thermal management strategies needed to obtain a roundtrip efficiency greater than 80%. System-level modeling and configuration studies have also focused on quantifying heat sources and heat sinks during forward and reverse operational modes, and gauging the importance of recycle streams from tail gases.

Introduction

The need for grid-scale electrical energy storage is becoming more acute as increasing amounts of intermittent renewable electrical sources come on line, making it increasingly difficult to match fluctuations in both supply and demand [1, 2]. Daily supply/demand cycles mean storage times of ~ 12 h, requiring the ability to store very large amounts of energy. Currently available methods generally fail to meet at least one of the main storage-technology criteria – cost, efficiency, storage capacity, durability, and widespread availability [1-4]. Hydroelectric water pumping and underground compressed air storage are well established but limited to specific naturally-occurring geographic sites. Secondary batteries and ultracapacitors currently have limitations for storing large amounts of energy cost effectively. Flow batteries may provide more scalable storage, although electrolyte volume and cost scale with energy stored [5, 6]. Reversible fuel cells have received only limited consideration for energy storage – although they have potential for large-scale storage, round-trip efficiency is usually relatively low [7, 8].

This project aims to demonstrate and develop a novel “Solid Oxide Flow Battery” (SOFB) for large-scale energy storage. This unique device occupies a new space that has similarities to, but is quite distinct from, both solid oxide fuel cells and flow batteries. The devices are different than flow batteries since the storage fluids are gaseous rather than liquid and the operating temperature is higher. They are also different than solid oxide fuel cells, as they operate reversibly rather than in one current direction, and at lower temperature and higher pressure.

Figure 1 shows a simplified schematic of the proposed SOFB energy storage system. The membrane-electrode assembly (MEA) is based upon ceramic components that are designed to operate at 600-750°C. In solid-oxide fuel cell (SOFC) mode, electricity is produced (discharge) as the fuel flows from the “SOFC Fuel” tank through the MEA, with the exhaust collected in “SOEC Fuel” tank. In solid-oxide electrolysis cell (SOEC) mode, the flow reverses direction, with electricity stored chemically (charging) in the “SOFC Fuel” tank. Oxygen flows through the lower channel. Oxygen ions are transferred through a dense ceramic membrane within the MEA.

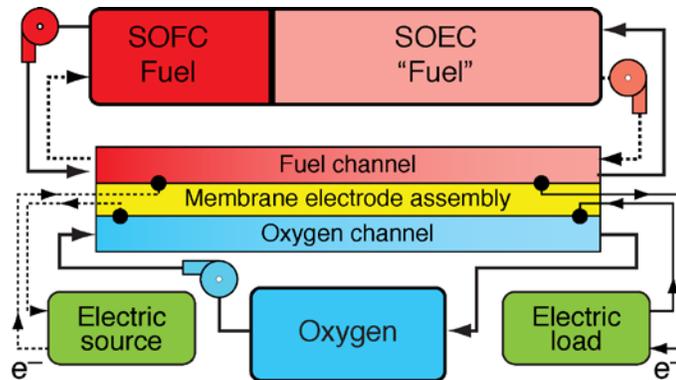


Figure 1: Simplified process flow diagram for the SOFB concept. Discharging is shown with solid lines and charging with dashed lines.

In conventional high-temperature H₂O or CO₂ electrolysis, relatively high electrolysis voltages are used to provide the input energy needed to compensate for the highly endothermic reactions. This ultimately leads to relatively low round-trip storage efficiency. Our SOFB concept is designed to overcome efficiency limitations by altering the products of electrolysis of H₂O-CO₂ mixtures. That is, by producing CH₄ in addition to H₂ and CO, the overall reaction becomes less endothermic, allowing lower electrolysis voltages and higher efficiency. In our proposed method, CH₄ production is increased by operating the SOFB with a C-H-O fuel-gas mixture at either (1) a relatively low temperature of $\approx 600^{\circ}\text{C}$ and 1 atm, or (2) an increased pressure of 3-15 atm and a more usual operating temperature of $\approx 750^{\circ}\text{C}$.

With the above unique approach used to improve efficiency, the SOFB has the potential to meet the desired large-scale energy storage criteria and also has some unique advantages:

- High round-trip efficiency;
- Large amounts of energy can be stored over time scales of hours or days, limited only by the size of the storage tanks, and yet the SOFB system can also respond quickly;
- Reasonable cost: using current cost targets for solid oxide fuel cells and an energy storage time of 12 h yields a very desirable stack cost for energy storage of approximately \$70/kWh;
- Solid electrolyte and tank leakage are minimal, yielding negligible energy loss during storage;
- The technology should have minimal environmental impact and uses mostly abundant and non-toxic materials of construction.
- SOFBs will integrate into the electrical network similar to other electrochemical storage devices; since energy is stored primarily as methane, they have the additional unique feature of allowing integration with the natural gas network;
- SOFB technology development will benefit substantially by leveraging prior/current development of solid oxide fuel cells, that has already advanced towards establishing good long-term stability, a route to low-cost large-scale manufacturing, and scale-up with > 100 kW demonstrations;

Given that no other widely available technology meets all the requirements, this innovative concept has the potential to be a game changer and play an important role in enabling extensive use of renewable energy. However, the technology will require substantial development from the state of the art in the closely related technology – solid oxide fuel cells. As noted above, SOFB requirements are significantly different than fuel cells, due to the unique operating conditions (low temperature and/or high pressure) and the need to work reliably upon many cycles between charge and discharge mode. This requires fundamental new cell materials development work, along with development of novel stack and system designs.

The research project aims to validate that the SOFB concept can yield high efficiency, and greatly extend current knowledge on solid oxide cell operation at high pressures and low temperatures. New cell materials, microstructures, and designs are being developed.

State-of-the-art methods for observing materials evolution during accelerated testing are being employed to assess and improve long-term stability. The work benefits from synergies between innovative cell development, experimental evaluation, fundamental physically-based modeling at the cell and stack level, and system-level modeling including balance-of-plant performance. Achieving high efficiency while producing enough excess heat to offset thermal losses and maintain the stack operating temperature ultimately depends on combined cell/system optimization. Thus, cell/system modeling is employed to guide cell performance targets and materials development in a concurrent R&D engineering approach that is expected to accelerate technology development.

The research is intended to provide sufficient proof-of-concept data to justify further investment in larger-scale development and implementation; the next stage would be development of a moderate-scale (~ kW) device. If expected targets are reached, the technology is anticipated to compete quite effectively against other storage technologies, providing strong motivation for commercial development.

Background

The field of energy storage using solid oxide cells continues to grow. Much of the work is on unidirectional cell operation, converting input renewable energy into chemical fuels. The group at Danish Technical University (Energy Conversion Department) continues to lead this field; a recent publication [9] provides interesting new insights into electrolysis durability. Two of us (Braun and Barnett) recently (April 2013) gave invited talks at a workshop held there titled: “Electrolysis and CO₂-Recycling for Production of Green Fuels (<http://indico.conferences.dtu.dk/conferenceDisplay.py?confId=131>). This area, along with that in the broader field of solid oxide fuel cells, is important because it improves the science and technology background supporting the present work.

Outside of our group, there has been relatively little work published related to the use of solid oxide cells for reversible electricity storage, but we are seeing increased activity at scientific conferences.

Results

Materials and Cell Development

Development of solid oxide cells (SOCs) that can work at the reduced operating temperature of < 600C (used to improve storage efficiency) have continued. In our prior report, novel SOC with thin (La,Sr)(Ga,Mg)O₃ (LSGM) electrolytes were described. These cells yielded the highest SOC power densities at ≤ 600C ever reported, e.g., >1 W/cm² at 550°C [10, 11]. The cell area specific resistance of < 0.2 Ωcm² is highly desirable for efficient energy storage. However, LSGM is not an ideal material for the thick physical support layer of the cell. Although details of the mechanical properties are not known, anecdotally the cells are relatively fragile. In addition, the use of thick LSGM supports is cost-prohibitive, given that Ga is comparatively expensive [12]. Finally, having an electronic conductor (versus ionically-conducting LSGM) as the support is more beneficial so that it can contribute to electrode current collection (the prior cells relied on the impregnated Ni for current collection) [13, 14]. This report

details results on a more practical next-generation cell that employs an electronically-conducting $(\text{Sr}_{0.8}\text{La}_{0.2})\text{TiO}_3$ (SLT) support that utilizes reasonably low-cost abundant materials. The current-voltage characteristics of the SOC in fuel cell mode show that the resistance at 600°C is $\sim 0.4 \Omega\text{cm}^2$, worse than the prior all-LSGM cells, but this can be improved by the use of an improved air electrode.

Since the air electrode is often a dominant resistance contribution to the SOC, its optimization is important. In the above-mentioned cells, the $(\text{La,Sr})(\text{Fe,Co})\text{O}_3$ air electrode limited cell performance, whereas our best cells have utilized a nano-scale $(\text{Sm,Sr})\text{CoO}_3$ air electrode. Work has continued to explore better air electrodes. One example is a relatively new class of promising Ruddleson-Popper phases. We have carried out initial work with electrodes impregnated with one such compound: Pr_2NiO_4 . X-ray scans of the impregnated material after firing in air at 1000°C show that the desired phase was obtained. Impedance measurements of a symmetrical air-electrode cell yielded a polarization resistance of $0.19 \Omega\text{cm}^2$. This is the first time that this material has been prepared by impregnation, and the low polarization resistance is very promising for an initial result.

Reduced-temperature firing is being developed as a new processing route to SOCs that can operate at or below 600°C . These cells would utilize doped ceria, an alternative to LSGM that has slightly better conductivity. The problem with ceria is its electronic conductivity that reduces open-circuit voltage and would result in a substantial efficiency penalty in an energy-storage application. In order to avoid this problem, some researchers have employed ceria-zirconia bi-layers, using the zirconia to block electronic current. Unfortunately, it has been difficult to process such thin bi-layer electrolytes because of interdiffusion between the two materials during sintering. Our novel process, which reduces firing temperature from 1400 to 1250°C by using fine-scale starting powders and Fe impurity as a sintering aid, is important because the reduced temperature minimizes ceria-zirconia interdiffusion. Early results from this development are quite promising. SEM images of the active region of the SOC show the Ni-YSZ fuel electrode, dense YSZ layer, dense Gd-doped ceria (GDC) layer, and LSCF air electrode with the desired microstructures. In cells to date, the YSZ layer was thicker than GDC, but in the future GDC will comprise most of the electrolyte thickness, with the lower-conductivity YSZ layer shrunk down to $\geq 1 \mu\text{m}$. The cell electrochemical characteristics show a low electrolyte resistance, important because this indicates minimal ceria-zirconia interdiffusion. Open-circuit voltage is high, indicating minimal electronic conductivity.

In order to utilize this approach for reduced-temperature SOCs, it will be necessary to make the low-conductivity YSZ layer much thinner, and the high-conductivity GDC layer somewhat thicker. The lower firing temperature should also enable the formation of Ni-YSZ fuel electrodes with smaller particle sizes, which will also facilitate good low-temperature performance.

Measurement System Development

The high-pressure electrochemical testing setup, pictured in Figure 2, has been installed and undergone successful initial tests under pressure. The first test data is expected shortly.



Figure 2. High pressure test setup, with grad student Gareth Hughes

SOFB Durability Testing

While Solid Oxide Cells (SOCs) have been developed and tested extensively for applications as Solid Oxide Fuel Cells and Solid Oxide Electrolysis Cells, there has been little attention to the Solid Oxide Flow Battery application proposed in the present project, where the device stores electricity by switching current directions periodically. Thus, it is critical to determine whether this operation mode affects device durability.

Among the degradation issues observed in SOCs, perhaps the most destructive is the delamination of the air-electrode observed during electrolysis operation. Many researchers have reported this issue, and a number of different theories behind the mechanism have been reported [15-17]. Our initial investigation into durability of SOCs in reversible operation has thus focused on the air-electrode; the most common such electrode, $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.98}\text{MnO}_3 - \text{Zr}_{0.84}\text{Y}_{0.16}\text{O}_2$ (LSM-YSZ), was studied.

The electrodes were screen printed on dense YSZ pellets and fired at 1175°C for 1 hour to produce symmetrical cells. All cells were tested and operated at 800°C in laboratory air. Current densities of 0.5 A/cm^2 or 1.5 A/cm^2 were applied to the cells, with the direction of current periodically switched abruptly to simulate reversible operation. Full cycle periods of 1 hour (30 minutes each direction), and 12 hours (6 hours each direction) were used. One cell was tested in single-direction current at 1.5 A/cm^2 as a control. Special care was taken to avoid the use of foreign current collector materials that can introduce artifacts in long-term tests [18].

Life test results for the cell operated at 1.5 A/cm^2 current in a single direction show that it degraded rapidly – when the test was stopped the total cell resistance had increased by 78%. Impedance spectroscopy analysis showed that both the ohmic and polarization resistance increased continuously during the test. Post-test SEM analysis revealed extensive delamination of the electrode maintained in electrolysis mode, while the

electrode maintained in fuel cell mode displayed no microstructural change. These results are in accord with prior reports for constant-current operation.[19]

The current-switching results provide interesting new insights. The cell tested at 1.5 A/cm² with 12 hour cycling showed degradation nearly identical to the control (dc current) sample. The ohmic and polarization resistances displayed similar behavior to the control sample, with both ohmic and polarization resistance increasing continuously. Post-test SEM analysis revealed delamination over significant portions of the LSM/YSZ interface. The delamination was observed at both electrodes, as expected since both electrodes were operated half the time at high current in electrolysis mode. Such delamination decreases the effective area of both the electrode and the electrolyte, explaining the observation that both ohmic and polarization resistance increased.

When the cycling period was reduced from 12 h to 1 h, keeping the current at 1.5 A/cm², the degradation rate was much reduced. The total resistance increase was again a combination of ohmic and polarization resistance. Post-test SEM analysis again showed delamination, but with a lesser fraction of the interface affected than for the 12 h cycle.

Life testing was also done for cells tested at a reduced current density of 0.5 A/cm², one with the 1 hour cycle and the other with the 12 hour cycle. Neither sample displayed an overall resistance increase over 1000 h, nor did post-test SEM analysis reveal any evidence of delamination, or any other microstructural changes.

In summary, degradation of cell performance in cyclic operation at high current can be related to the delamination observed by SEM, as observed in prior electrolysis-only experiments [20]. Furthermore, reducing the current density from 1.5 to 0.5 A/cm² led to no measurable degradation over 1000 hours of operation, regardless of cycling condition. This observation is extremely favorable for the proposed storage method, where the cells should be operated at relatively low current density and overpotential in order to achieve high round-trip efficiency. The other important result here is that no new degradation mechanisms are introduced due to current cycling; in fact, degradation appears to be decreased relative to constant-current operation. The present results, where degradation rate decreases with decreasing cycle period, suggest that there is an incubation time for the delamination process. This seems reasonable given that the proposed mechanisms [16, 17, 21] generally involve formation of a new phase or of a void in the electrode/electrolyte.

Physically Based Cell and Systems Modeling

Physically-based cell modeling plays a central role in the SOFB research effort, spanning from fundamental electrochemistry to stack performance. There are three main objectives associated with high fidelity cell modeling. One objective of this task is to develop and validate the fundamental theory and modeling framework of reversible solid oxide cells. Another primary objective is to extend fuel-cell models to include electrolysis operation and to represent new materials and cell architectures. Throughout the research effort, cell level modeling will be developed and applied to interpret and guide experimental investigations. In addition to new materials, it is anticipated that models will be extended and validated to represent high-pressure and low-temperature

operation. System models usually do not resolve micron-scale phenomena, however, gross performance (e.g., overall polarization characteristics) can be derived from detailed cell and stack-level models and used for system design. Thus, reduction of higher fidelity cell and stack models shall be performed for system-level design, simulation, and optimization.

The system level modeling, design, and analysis tasks seek to elucidate attractive system architectures that enable the high efficiency SOFB cell-stack (or tube bundle) performance to be retained. Additionally, system modeling interjects critical feedback into the SOFB materials/cell/stack research process by providing a holistic viewpoint that is cognizant of grid energy storage requirements and balance-of-plant constraints. Further, the systems R&D tasks focus on understanding scale-up design approaches and translating system-level requirements to material development efforts.

The past year's efforts have focused on fundamental thermodynamics of reversible cells at the button and cell-levels and dynamic cell-level model development. The dynamic cell-level model will eventually be employed as a design and simulation tool for stack and system studies. In the following, thermoneutral voltage studies at the button cell scale and reversible solid oxide cell (rSOC) model development are first summarized followed by continued systems-level configuration analysis.

Button-cell Studies

The thermal balance within the SOC system and the heat exchange with the environment plays an important role in achieving high cell performance and system efficiency. Consequently, we have dedicated effort at characterizing the heat balance on the cell and its impact on thermal management of the SOFB system. The heat exchange of the SOC system with the environment can be understood by analyzing the thermal voltage. If there is no heat exchange with the environment, the SOC is considered to be operated thermally neutral to the environment. If the solid-oxide cell is operating isothermally, and there is no net heat exchange with the environment (i.e., $\dot{Q} = 0$), then the solid-oxide cell is said to be operated thermoneutrally, at which, the operating cell voltage is called thermoneutral voltage, which is expressed as $E_{\text{TN}} = -\Delta H/I_e$. In terms of the thermoneutral voltage, the added heat from the environment to the system can be rewritten as,

$$\dot{Q} = -I_e(E_{\text{TN}} - E_{\text{cell}}).$$

Certainly, the thermoneutral voltage at the given inlet fuel and air streams depends on the compositions of the products at the outlet of the fuel and air streams, which in turns, depends on the current or the oxygen ion exchange rate (i.e., $J_{\text{O}^{2-}} = I_e/2F$) between the fuel and air streams. Ideally, the thermoneutral voltage at the given current can be evaluated unambiguously by assuming that the products at both the fuel and air stream outlets are in equilibrium state at the given temperature and pressure. However, practically, the products may not reach the equilibrium state depending on the reactant gas residence times, the material set, and catalyst area within the electrodes. Therefore, one motivation has been to understand the effects of the cell MEA microstructure and the operating conditions on the thermal balance with the environment.

A button-cell model considering the MEA microstructure has been used to analyze the effects of the cell structure and the operating conditions on heat exchange with the environment. The model is largely based on previous efforts and stirred reactors are used to represent the fuel and air streams [13, 22-24]. Figure 3 shows the polarization curve of the current density and electric power as functions of the operating cell potential spanning from the fuel cell mode to the electrolysis mode. The inlet fuel stream is an SOEC species composition established from system-level studies. The operating temperature and pressure are taken to be 800 °C and 20 atm, respectively. The enthalpy change ΔH considering both the fuel and air streams, and the heat exchange with the environment Q are also illustrated in Figure 3. The OCV is about 1.0 V. Below the OCV, the cell is operated under the fuel-cell mode, the positive current and the power are produced. The enthalpy of the fuel and air stream at the outlet is smaller than that at the inlet, the enthalpy change ΔH is negative. Because of the inefficiency of the SOC system, the enthalpy change is not fully converted into the electric power, and there exists heat release from the SOC system to the environment ($Q < 0$). As the voltage increases from the short circuit to the OCV, the current density decreases, the enthalpy change and heat release also decreases.

However, when the operating cell voltage is greater than the OCV, the SOC is operated under the electrolysis mode. The electric power becomes negative, which means that the electric power input is required to the system. Meanwhile, the enthalpy change becomes positive, the heat change with the environment is positive between the OCV and about 1.32 volt, and then becomes negative as E_{cell} is greater than about 1.32 volt. Because the heat exchange with the environment at about 1.32 volt is zero, the SOC is operated thermoneutrally, and thus the thermoneutral voltage is about 1.32 volt.

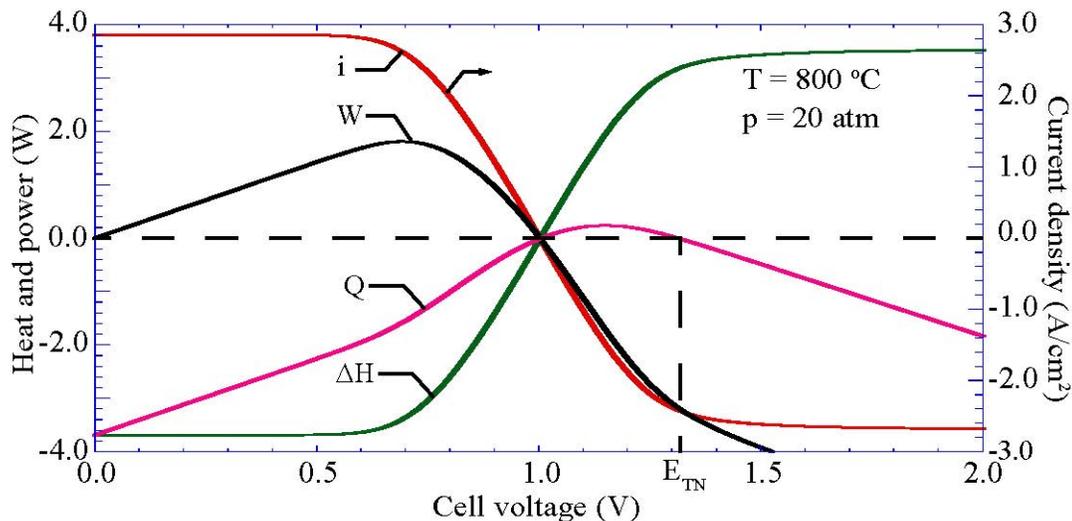


Figure 3. Profiles of the enthalpy change of the fuel and air stream, electric power, heat exchange with the environment, and the cell current density as functions of the operating cell voltage.

Figure 4 compares the heat exchange with the environment at four effective specific catalyst surfaces (m^2/m^3) within the anode microstructure. As the catalyst surface increases, the thermoneutral voltage (i.e., the voltage at which $\dot{Q} = 0$) becomes smaller, and is closer to the equilibrium thermoneutral voltage of 1.32 V previously established from Figure 3.

The important result here is that it is clearly possible to achieve non-equilibrium gas conditions within a cell and the point of cell thermoneutrality is then appropriately shifted as endothermic cell operation is balanced with exothermic methanation processes. Given that anode catalyst specific surfaces areas are on the order of 1000 cm^{-1} , considerations of non-equilibrium conditions and the associated affects on E_{TN} must be considered in the design and operation of the SOFB.

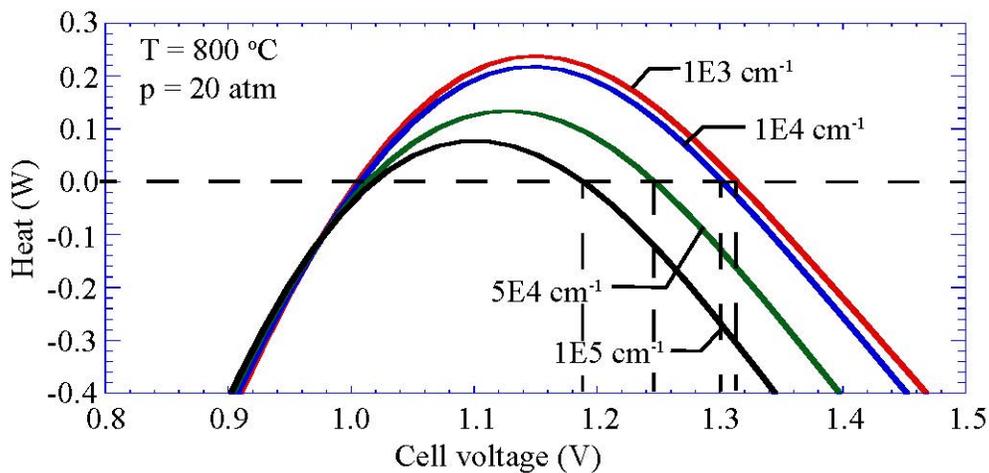


Figure 4. Heat exchange of the SOC button cells with the environment as functions of the operating cell potential at four specific catalyst surfaces within the anode microstructure: $1\text{E}3$, $1\text{E}4$, $5\text{E}4$, and $1\text{E}5 \text{ cm}^{-1}$.

Single-Cell and Stack Modeling of rSOCs

We view the development of a high fidelity cell-stack level model that can be employed to predict both steady-state and dynamic stack performance as a critical need in SOFB system design and optimization. In particular, one of the aims is to have a tool that enables quantitative predictions of changes in SOFB performance due to variations in SOC operating conditions (e.g., T , p , composition, utilization), and provides a quantitative basis for establishing desired tank storage state points (T , p , and composition), thermal management of the SOFB system, and operating strategies for load change and mode-switching. Thus, the research has focused on developing a high-fidelity, dynamic SOC stack simulation tool for the purposes outlined above. Modeling steady-state and dynamic behavior of solid oxide fuel cells (forward, power-producing) at both cell and system levels is well-established. However, in the reverse operational mode (i.e., electrolysis mode), both experimental and numerical prediction of solid oxide electrolysis cell (SOEC) performance has yet to be reliably established given its relative

technological infancy. As an intermediate step toward developing a sophisticated dynamic reversible SOC model and identifying favorable electrochemical and thermal performance of SOCs, recent efforts focused on the development of a steady-state and dynamic cell model for SOECs by improving and extending existing models to enable exploration of cell geometry, operating conditions, and feed gas effects. The model has been calibrated and validated versus available experimental and numerical data in the literature for various cell design fueled by steam and syngas. Throughout the validation cases, the model was also employed to investigate the effect of several parameters on performance and to provide insight for future research and development directions related to system design and optimization.

To simulate a planar SOEC, an interface charge-transfer channel model is developed and extended to represent an entire cell/stack model (see Figure 5). In the model, any combination of H_2 , CO , CO_2 , H_2O , CH_4 and N_2 is certainly possible as a feedstock gas mixture (cathode side in electrolysis mode). There is flexibility in setting the oxygen fraction in the anode channel inlet and the value ranges from the oxygen concentration in ambient air to pure O_2 .

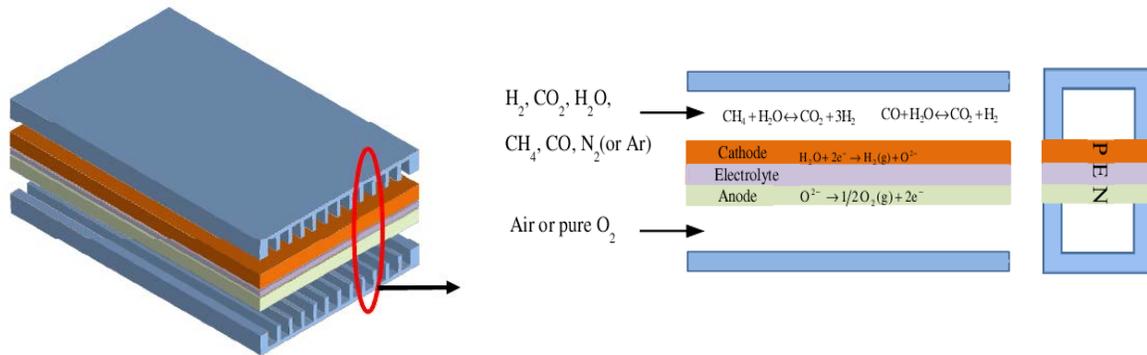


Figure 5. Representation of the SOEC stack is reduced to a channel in a single cell

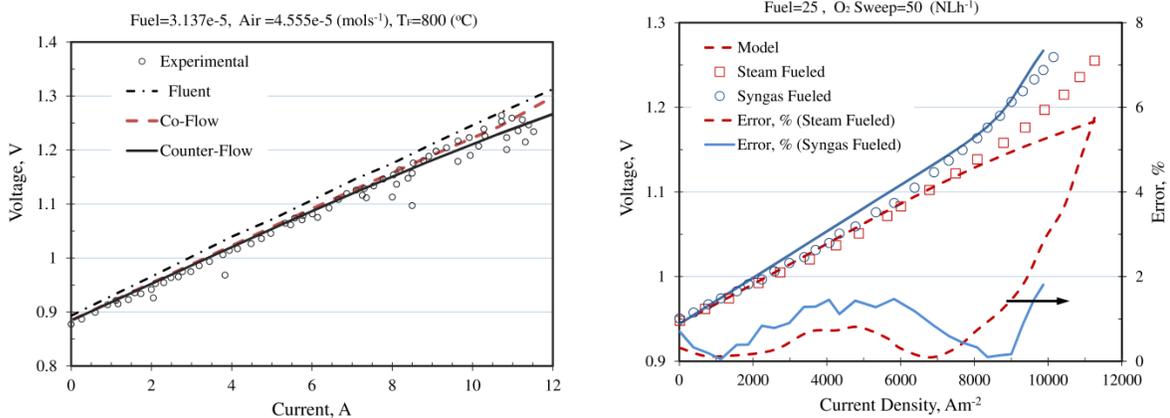
The model includes mass, energy, and momentum conservation equations for the configuration and inlet compositions outlines above. Global reaction rates for RWGS and methanation (i.e., reverse SR) reactions are also included in order to calculate the rate of CO_2 , CO , and CH_4 species production or consumption. To calculate the local temperature distribution along each individual channel, energy balances on each of the five cell layers are considered in the present model for predicting the local temperature distribution in the cathode and anode side interconnects, PEN, and anode and cathode flow streams. The model also includes complete evaluation of the cell electrochemical losses i.e., ohmic, activation and concentration polarizations.

One of the challenges in validating detailed models for the simulation of SOECs is the limited experimental data available in the extant literature, particularly for syngas-fueled SOECs. Even within the existing literature, detailed information regarding the distributed cell variables, such as current, temperature, and mole fraction, are rarely presented. Given these difficulties, our present approach focused on separate benchmarking of high- and intermediate-temperature SOEC performance as detailed in

the following. However, future cell data will come from the collaboration with the Barnett group at NU. For now, the model development and validation proceeded with a generalized methodology that will enable data from future pressurized testing of cells using LSGM-SLT and other material sets as being developed at NU.

The two sets of data that were selected in order to calibrate and validate the present model, were established from Refs. [25, 26]. The data sets contain experimental data for both button cell and a stack setup fueled by steam and syngas. From these experimental results, the SOEC model has been validated at both cell and stack levels with different fuels. The second set is from the Ref. [19] which is used to validate the model for IT-SOECs. This set of data also provides results illustrating the effect of syngas gas compositional mixture on the V-J characteristic curve. For both HT-SOECs and IT-SOECs, the model is firstly calibrated based on the experimental data, using ohmic (including the contact resistance) and activation polarization parameters as the fitting parameters. The model is, then, employed for validation purposes by fixing the fitting parameters, changing the operational and geometrical parameters, and finally comparing with available experimental data.

As a validation example, Figure 6(a) compares model predicted results in co- and counter-flow configurations with experimental data in cross-flow design for an HT-SOEC. Fluent results given in Ref. [27] are also shown in the same figure for comparison. Although the current is negative at the electrolysis mode, its absolute value is considered here. As can be seen, the predicted values are acceptable in comparison with experimental and Fluent results and the general shape of the voltage-current density (V-J) characteristic curve is quite similar. The present model can also precisely estimate the open circuit voltage of the cell ($E_N = 0.8864$ V). The models tend to over-predict the polarization somewhat, particularly at low current. Since the activation overpotential is neglected in the Fluent model, the cell voltage is higher at each current value. Differences between co- and counter-flow results are related to the temperature distribution inside the cell as shown in Fig 6(a).



(a) Steam fuelled SOEC stack

(b) Steam and syngas fuelled IT-SOEC

Figure 6. Comparison between experimental and numerical results

Fig. 6(b) depicts an example of the model validation for IT-SOECs when the fuel flow contains 50% H₂O-50% H₂ and 25% H₂O-25% H₂-25% CO₂-25% CO gas mixtures. The maximum deviation of the numerical result from the experimental data is shown to be about 6% at a current density around 10300 Am⁻². In the low current density operating range (0–5000 Acm⁻²), which is the dominant operating range of SOECs, the difference between numerical and experimental data is negligible at less than 1%. In summary, the numerical model results for steam and syngas fueled IT-SOECs, have demonstrated good agreement with the experimental data even in the high current density ranges.

Several other cases for both steam and syngas fueled HT- and IT-SOECs are also investigated as a part of the model validation effort (e.g., with changing the inlet fuel compositions, cell geometry, etc.), some examples are presented in the next section through parameter study. In spite of the fact that a 1-D model is employed in this study (which is the more appropriate approach for the system study), there are several reasons that are recognized for the minor differences between the model results and the experimental values, especially in the high voltage operating range. The primary reasons for model discrepancy are due to (1) contact resistances within the experimental cell-stack (as described below), (2) estimation of the activation overpotential (as described below), and (3) the cross-flow configuration of the test article versus the parallel flow configuration employed in the model.

Several studies [28, 29] show the voltage vs. current density for SOEC stacks is significantly below those results presented for button and single cells. Therefore, it can be argued that beside the major cell overpotentials (i.e. ohmic, activation and concentration), the contact resistances (in magnitude order) between the electrodes and the current collectors, at the interfaces between the electrodes and the electrolyte, and the resistance of the wiring are very important. In some recently reported experimental studies, 60% (or even more) of the overall losses are estimated to belong to the above resistances [27]. Therefore, reliable single cell or stack models must consider the effects of these resistances (which are not constant during operation). The overpotential related to these resistances can be even higher than all of the other cell overpotentials.

In almost all of the validation cases, it was observed that the determination of activation polarization is a challenge in developing reliable SOEC models in the desired operating range for SOFB (i.e., at low-to-modest current density). Therefore, either experimental measurements or more detailed models that include distributed charge transfer modeling such as that of Moyer et al. [30], or improved Butler-Volmer representations that include competitive CO₂ electro-reduction for channel-level, interface charge-transfer models of SOECs are needed. However, the employed fidelity in the present model development effort meets the project requirements for systems-level studies.

Model predictions for varying inlet temperature and composition are given in Figure 7 for a single cell SOEC. The results show that the operational voltage of the cell is weakly related to the inlet steam concentration. Since the power consumption of the SOEC is a strong function of the fuel flow rate to the stack (or steam level), it is very

important to keep the steam level to a minimum value (that is a function of several parameters, such as the cell size) during the electrolysis process.

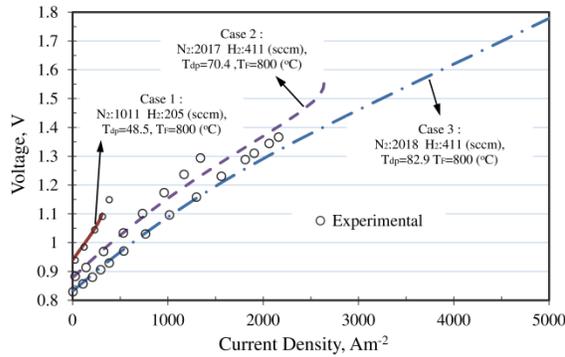


Figure 7. Effects of inlet flow temperatures and gas compositions on performance characteristic curve of a steam fuelled button cell

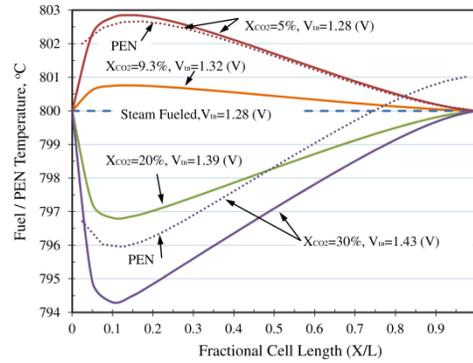


Figure 8. Fuel, Air and PEN temperatures profiles along the channel length at thermoneutral voltage

Another important modeling consideration is whether CO_2 species are electrochemically reduced or preferentially participate in the reverse water-gas shift reaction. While not shown, good agreement between the experimental and numerical shows that assuming the reverse WGS reaction as the main pathway for CO_2 consumption is an appropriate modeling approach given sufficient water vapor is present. Additionally, the impact of reactant flow configuration (co- or counter-flow) was also investigated and found to adequately represent cross-flow stacks.

Figure 8 presents the fuel, air and PEN temperature profiles along the channel length at a thermoneutral voltage condition. Even at this voltage, the interior node temperatures deviate from the inlet condition due to the RWGS and methanation reactions. The thermoneutral voltage estimated by the model is about 1.32 V for both co- and counter-flow configurations. Values between 1.30 to 1.34 have been measured through experiment [31]. Fluent-based modeling also shows a thermoneutral voltage value near 1.34 V [31]. Due to endothermic nature of RWGS reaction at near ambient pressures, more heat needs to be generated through the electrochemical reactions in order to have a thermoneutral condition. Therefore, the thermoneutral voltage is higher for a syngas-fueled SOEC than pure steam electrolyzer even if the CO_2 electrolysis is neglected. The exothermic nature of the methanation reaction alters the thermoneutral voltage value especially at higher operating pressure.

In conclusion, the project effort thus far has demonstrated that the developed model can readily predict the SOEC performance for a variety of operating conditions (cell temperatures and inlet gas compositions) and operational current densities for both cells and stacks. The model also sufficiently demonstrates the desired fidelity requirements and predictive capability to support the systems studies and configuration analyses.

System Modeling, Design, and Analysis

The past year's research has also continued to focus on analyzing system concepts and the gas storage and thermal management strategies needed to obtain a roundtrip efficient greater than 80%. This effort has primarily employed models that are not as high fidelity as previously discussed. Figure 9 shows the system concept that has been under study. Figure 9(a.) depicts the operation when the battery is charging (electrolysis mode – 'EC mode'). Feed gases rich in H_2O and CO_2 are discharged from the EC tank at state (2), preheated by the stack discharge gases, and enter the stack (3) where with a supply of electric energy from a source, such as wind turbine or PV array, they are converted to a fuel-rich (H_2 , CO , CH_4) stream at state (4). Figure 9(b.) depicts the discharge (fuel cell mode – 'FC mode') operation. The FC gases are discharged from the FC tank at (2), preheated by the discharge gases from the fuel electrode, and enter the stack at (3). The stack electrochemically oxidizes the fuel producing DC power and H_2O and CO_2 gaseous products.

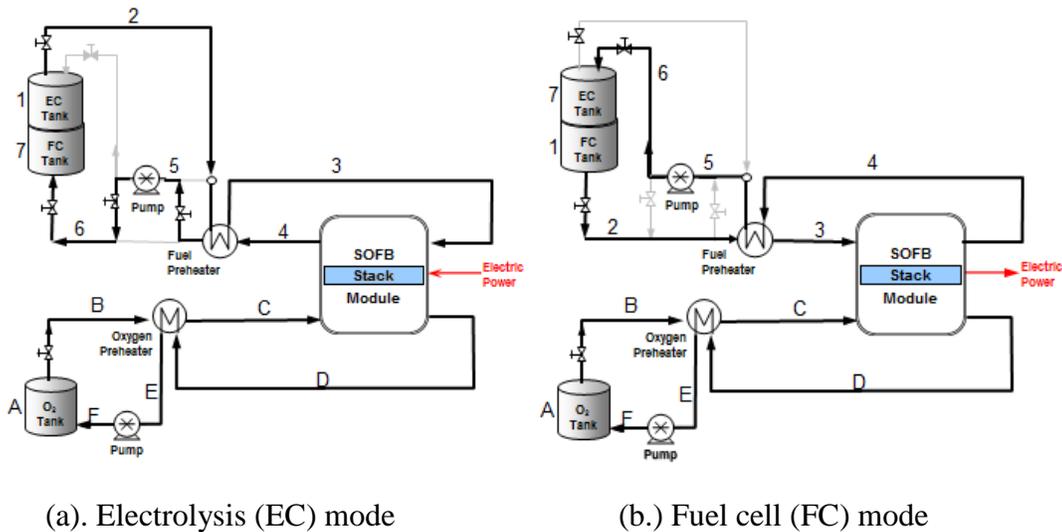


Figure 9. Basic system concept for the solid oxide flow battery

Thermoneutral Voltage Considerations

One challenge in the design of this system is that the operating conditions that are most favorable for an SOFC are not necessarily desirable for an SOEC. This challenge, as well as the complex and interrelated system-level impact of altering stack operation conditions, was apparent during initial system simulations. In an effort to proficiently design such a system the thermoneutral voltage is employed to assess desirable operating conditions. The effect of thermoneutral voltage on operating conditions such as temperature, pressure, fuel utilization, and fuel composition is understood through sensitivity studies.

The roundtrip system efficiency for an SOFB is defined as the quotient of net energy generated in SOFC mode (discharging) to the total power supplied in SOEC mode (charging). This efficiency parameter is impacted by both the electrical power supplied

to and generated by the rSOC stack, as well as the balance of plant (BOP) power requirements (i.e. compressors and process flow streams). To achieve high roundtrip system efficiency, it is important to minimize the BOP energy as well as operate the rSOC stack efficiently (i.e. at low overpotential). The roundtrip stack efficiency is plotted as a function of overpotential in Figure 10. The roundtrip stack efficiency neglects the effect of balance of plant power requirements. In order to reach a targeted roundtrip system efficiency of 80%, while allowing for 5% efficiency loss attributed to the BOP power requirements, an overpotential of 85 mV is the maximum allowed in both modes of operation.

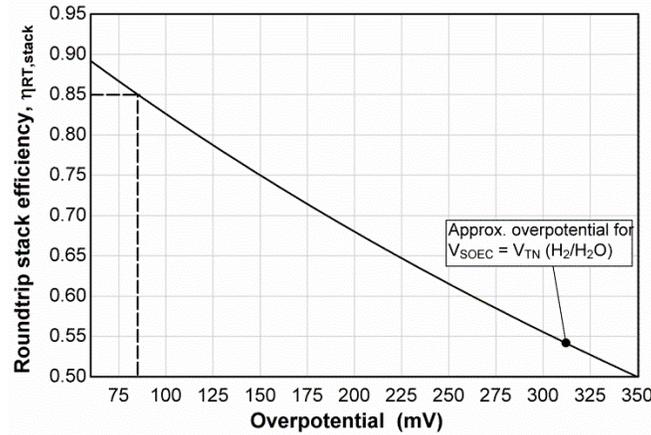


Figure 10. Roundtrip stack efficiency vs. overpotential assuming equal overpotential in both modes.

The BOP energy requirements are closely related to the heat generated or consumed by the rSOC stack in each mode of operation. For example, surplus heat generation by the rSOC is often offset by excess oxidant cooling flow which increases the power required by the oxidant compressor. Additionally, for self-sufficient operation, the rSOC stack must generate enough heat in both modes of operating to account for losses to the environment and other system processes (i.e. preheating inlet streams).

As has been previously discussed, the thermoneutral voltage, V_{TN} can be used to thermodynamically predict the net heat generated by the rSOC stack. The heat-to-power ratio in an rSOC is estimated as $\dot{Q}/\dot{W} = 1 - V_{TN}/V_{cell}$. Large differences between V_{TN} and V_{cell} result in large magnitude heat generation or consumption by the stack, which negatively impacts BOP power requirements.

The thermoneutral, Nernst, and operating voltages are plotted as a function of operating pressure for a carbonaceous fuel in Figure 11. As the pressure increases, the extent of methanation in the SOEC increases causing the thermoneutral voltage to decrease. Additionally, the Nernst voltage increases slightly with pressure.

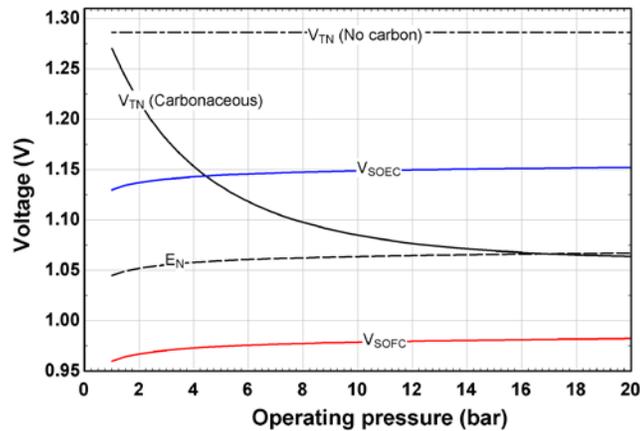


Figure 11. Thermoneutral voltage, Nernst voltage, and cell voltages (V_{SOFC} , V_{SOEC}) vs. operating pressure assuming a constant overpotential of 85mV in both modes of operation

The heat-to-power ratio is plotted as a function of pressure for SOEC mode in Figure 12(a). At low pressure, additional heat is required to maintain the rSOC operating temperature because the endothermic electrolysis process is the most significant reaction. The heat-to-power ratio increases with increased pressure for the carbonaceous fuel because exothermic methane formation is promoted at high pressure. The rSOC becomes thermoneutral at 4.5 bar and generates net heat at higher pressures. The increase of the heat-to-power ratio with pressure corresponds to a decrease in the thermoneutral voltage (see Figure 11). Additionally, the thermoneutral condition is satisfied when the thermoneutral voltage is equal to the operating voltage ($V_{\text{SOEC}}=V_{\text{TN}}$). The rSOC operated with a carbonless fuel composition cannot form methane. Consequently, the thermoneutral voltage is constant with pressure and the stack requires additional heat even at high pressure.

Fig. 12(b) shows the heat-to-power ratio in SOFC mode as a function of pressure. At low pressure the rSOC generates a significant amount of net heat, which negatively impacts the BOP power. As pressure increases, the heat-to-power ratio for the carbonaceous fuel decreases because an SOFB system operating at high pressure has a high concentration of methane at the SOFC mode stack inlet, leading to internal endothermic steam-methane reforming. The carbon-less fuel maintains an unfavorably high heat-to-power even at high pressure.

The relationships between rSOC operating conditions, thermoneutral voltage, and heat-to-power ratio provide a foundation for understanding and predicting desirable operating conditions. Lower heat-to-power ratio is achieved in both modes of operation when the thermoneutral voltage is reduced. By reducing the thermoneutral voltage to a value near the Nernst voltage (i.e. $E_N=V_{\text{TN}}$), the rSOC stack generates a relatively small amount of heat in both modes that can be efficiently removed from the stack and used in other system processes.

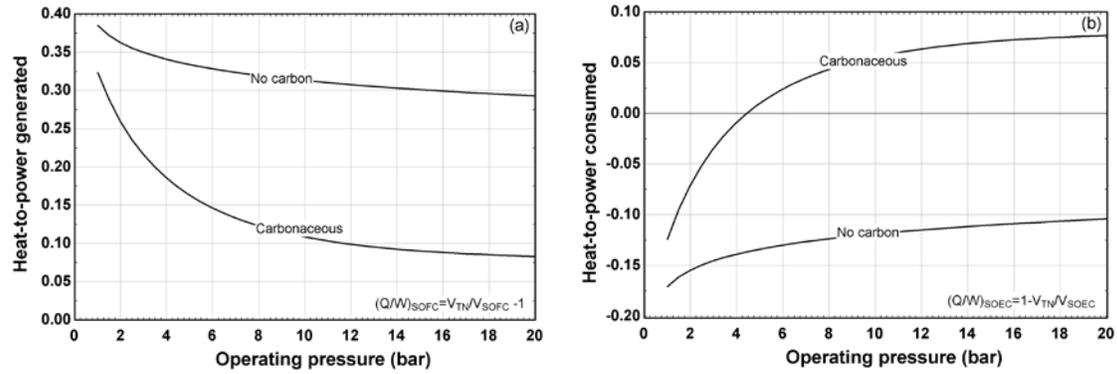


Figure 12. Heat-to-power ratio vs. operating pressure in (a) SOEC mode and (b) SOFC mode for carbonless and carbonaceous fuel compositions at $T=750^{\circ}\text{C}$, $U_f=50\%$.

The methods used to determine the pressure dependence of thermoneutral voltage are extended to other rSOC operating parameters, specifically temperature, fuel utilization, and the inlet fuel composition. In general, the thermoneutral voltage is reduced through increased pressure, reduced temperature, reduced fuel utilization, and reduced hydrogen-to-carbon ratio. Several combinations of these operating conditions are revealed to be possible for an SOFB system. For example, the desirable operating point where $V_{\text{TN}} = E_N$ is satisfied for both high temperature and high pressure operation ($T=800^{\circ}\text{C}$, $p=20\text{bar}$, $U_f = 45\%$, hydrogen-to-carbon ratio = 10) and low temperature and high pressure operation ($T=600^{\circ}\text{C}$, $p=20\text{bar}$, $U_f = 72\%$, hydrogen-to-carbon ratio = 6). The low temperature conditions are expected to further reduce the BOP energy requirements because of the higher fuel utilization; however, this requires a highly efficient low temperature rSOC.

Awareness of the effects of operating conditions on the thermoneutral voltage parameter will be instrumental in understanding the results from higher fidelity studies that employ current-voltage performance characteristics, finite reaction kinetics, and local temperature gradients within the rSOCs. These studies are essential for quantifying the system efficiency and economics of the proposed SOFB system. For example, this study predicts that lower stack temperature reduces BOP power requirements. However, if lower overpotential is possible with a high temperature stack, the roundtrip system efficiency may benefit from higher temperature.

Systems Modeling and Configuration Analysis

Systems-level modeling and configuration studies have continued in the past year with a focus on quantifying heat sources and heat sinks during forward and reverse operational modes, and the gauging the importance of recycle streams from rSOC tail-gases. The focus has been on relatively small SOFB systems on the order of 10 – 15 kW of stack power with gases being stored in each mode of operation, however, one of the objectives will be to perform scale-up studies to understand relationships between energy storage efficiency, energy storage capacity, and tank sizing. Importantly, simulated SOFB systems continued to achieve roundtrip stack efficiencies near 80% and small-

scale system simulations reveal some of the potential operating challenges while providing information that will be useful in designing a grid-scale SOFB system.

Progress

Renewable electricity sources such as wind and solar are the primary alternative to fossil-fueled generation, and hence are critical for greenhouse gas reduction. However, the intermittent nature of these sources poses a formidable barrier to their adoption at significant fractions of our total electricity production. Thus, efficient and low-cost grid-scale energy storage must be a key part of plans to reduce greenhouse gas emissions. Although the technology being developed in this project is new and needs validation at many levels, it is still potentially important given that currently available storage methods generally fail to meet at least one of the main storage-technology criteria – cost, efficiency, storage capacity, durability, and widespread availability. The results obtained in the past year have filled in many important details regarding SOFB materials and characteristics, and system design. Particularly important are the observations that practical reduced-temperature SOCs can be made, reversing cell operation does not introduce new degradation mechanisms, that degradation is eliminated for the moderate current densities that are consistent with high efficiency, and that increasingly realistic cell/stack/system level models show that round-trip efficiencies near 80% are feasible. Overall, the results continue to show good promise for this technology.

Future Plans

Stability studies of cells designed for high pressure, high temperature operation will focus more on the fuel electrode, as the oxygen electrode has already been characterized. Now that the pressure testing capability is online, the durability testing will be extended to pressurized conditions, an area where there is little or no data in the literature. Now that the cells for reduced temperature operation have been fully developed, their durability testing will be done over the upcoming year. Exit-gas constitution measurements will be analyzed to reveal whether the fuel electrode has sufficient catalytic activity to produce a near-equilibrium product. The cell-level modeling capability will increasingly be used to assist in the quantitative interpretation of experimental cell-test results and help guide experimental lines of investigation.

Cell- and stack-level models developed in the past year, informed by experimental cell test data taken under realistic operating temperature and pressure conditions, will be employed in the systems models, making them quite realistic. Further work at the system-level will address optimal system configurations with consideration to gas-storage strategies, water separation for storage, auxiliary reactors, gas recycle loops, and heat exchangers. Scale-up and viable energy storage system strategies will be explored. Additionally, particular emphasis will be given to concurrent engineering of material set development and systems development.

Publications and Patents

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