REVERSE FUEL CELL OPERATION ON LOAD CHANGE:
MODEL AND EXPERIMENTAL STUDY

Randall S. Gemmen, Christopher D. Johnson, James A. Poston, Jr.
National Energy Technology Laboratory, U. S. Department of Energy
3610 Collins Ferry Rd., Morgantown, WV 26507, USA

ABSTRACT

Achieving safe and reliable transient solid oxide fuel cell (SOFC) operation is important for many power generation applications. To date, most reported studies on transient loading are presented as a minor aspect of other steady state performance studies. In addition, only a few modeling studies on the electrochemical performance of SOFCs have been reported, and in these only for relatively small load changes. In this paper we review recent model results examining the transient performance of three common SOFC geometries (cross-flow, co-flow, and counter-flow) during large load/unload events. Of particular note for large load decrease conditions (e.g., shutdown) is the occurrence of reverse current over significant portions of the cell, starting from the moment of load loss up to the point where equilibrated conditions again provide positive current. Test results of a button cell operated under reverse current are also reported to help begin to identify what effects such operation may have on fuel cell performance and durability.

INTRODUCTION

Most of the focus in the development of fuel cell technology is on achieving good steady state performance. Good performance includes not only good fuel to electric conversion efficiency, but also long lifetime (e.g., >40,000 hr for stationary applications). While good steady state performance is critical for the commercialization of fuel cell technology, dynamic performance is also important, particularly at the low power range (~3 to 30 kW) where purchasers expect backup power capability. Numerous investigators have examined the overall performance of fuel cell systems, and some have examined system dynamics due to load changes (e.g., 1-5). However, at least for SOFC technology, very little has yet been done to examine what occurs within the cell/stack due to load variations (6-8). As SOFC systems mature, showing steady state performances viable for commercialization, attention will need to turn to how these systems will safely support load following capability, as well as other dynamic events such as load trips and emergency shutdowns that can be expected when under service.

At the National Energy Technology Laboratory (NETL), work is underway to examine cell and stack dynamic performance. Both models and experimental work are being pursued. This paper reviews recent model results showing the performance of SOFC fuel cells during large load changes, which shows the existence of current reversal (electrolysis) over portions of the cell for sufficiently large load loss (9). Such current reversal is found to exist regardless of cell geometry: co-flow, cross-flow, and counter-
flow. The paper also reports on recent experimental work showing the performance of SOFC button cells during current reversal.

MODELING SOFC DYNAMIC PERFORMANCE

Details of the model used to generate the results presented here are available in (9). In short, the model can be applied to investigate a wide range of transient cell behavior (at electrochemical timescales, up to thermal transient timescales). For this work the model is applied to specifically investigate the thermal transient cell behavior following load changes. Because thermal behavior occurs at long timescales, in this work gas flows and electrochemistry are considered quasi-steady. A generic bi-polar, planar fuel cell is examined - see Figure 1. Straight, single pass flow channels are assumed to evenly distribute fuel and oxidant to the fuel electrode and air electrode sides of the cell, respectively. Regardless of flow geometry, co-flow, cross-flow, or counter-flow, these flow channels can be analyzed using one-dimensional flow calculations to provide useful design information (10). The justification for using the one-dimensional transient flow calculations used in the present study can be found from an analysis of the characteristic timescales of an SOFC fuel cell as discussed in (9). There, too, we report the success of model validation using experimental cell transient data. In addition, the model was verified by comparing its results to that of the National Fuel Cell Research Center and found to be comparable (11). The model was also tested in cross-flow geometry by comparing results to that of others and the results were the same to within 4% (10).

The model was applied to investigate three cases of planar 10 cm x 10 cm fuel cell design (co-flow, cross-flow and counter-flow). For these three cases, the model input parameter values provide cell steady state performances close to what is anticipated for the SECA Program fuel cell systems (12). In particular, at a cell voltage of 0.77 volts and fuel and air utilizations of 0.81 and 0.11, respectively, cell average current density was about 0.74 A/cm². The cells were assumed to have a 10 cm x 10 cm active area, so the channel lengths for both fuel electrode and air electrode are 10 cm long. Eight channels are used for both the fuel electrode and air electrode, and each channel has eight nodes—which has been found in other work to be sufficient to resolve the behavior of the cell with near node independency (13). The resultant size of each node is 12.5 mm x 12.5 mm. Time steps used in the solution of the model ranged from 3.0E-2 to 8.0E-2 sec, which was

![Figure 1. Planar cross-flow cell geometry.](image-url)
controlled by the solution of the solid phase thermal transient (the gas was assumed quasi-steady).

For each cell geometry, several load transients were imposed that are representative of real world applications, especially complete load loss. As reported elsewhere, large load losses can induce current reversal over portions of the cell (9).

**Model Results**

Results from the study examining load loss dynamics for each of the three geometries are shown in Figures 2a through 2d. For all cases, the same type of load change was imposed, namely forcing the cell voltage to change from 0.70 to 0.96 volts.

![Figure 2a. Contour of current reversal (Cross-flow).](image)

![Figure 2b. Contour current reversal (Counter-flow).](image)

![Figure 2c. Contour of current reversal (Co-flow).](image)

![Figure 2d. Contour of Nernst potential (Cross-flow).](image)

Figure 2a shows a contour plot of the current density for the cross-flow case immediately following load loss. As can be seen, a significant portion of the cell experiences a negative current condition following the strong load decrease. Close examination of the model data at this time show that the peak negative current density achieved on the cell is
about \(-1330\) A/m\(^2\). The average cell load current density at this time is about \(-9\) A/m\(^2\) (essentially zero).

Figure 2b shows a contour plot for the counter-flow case of the current density immediately following load loss. Again, a significant portion of the cell experiences negative current conditions over a lengthy duration as the cell slowly thermally equilibrates to its new steady state condition. Close examination of the model data at this time show that the peak negative current density achieved on the cell is about \(-1060\) A/m\(^2\). The average cell load current density at this time is about \(350\) A/m\(^2\). Hence, for the load loss conditions studied here, where the cell voltage changes from 0.70 to 0.957 volts, counter-flow geometries do not loose load completely.

Figure 2c shows a contour plot for the co-flow case of the current density immediately following load loss. Again, a significant portion of the cell experiences negative current conditions over a lengthy duration as the cell slowly thermally equilibrates to its new steady state condition. Close examination of the model data at this time show that the peak negative current density achieved on the cell is about \(-690\) A/m\(^2\). The average cell load current at this time is about \(-74\) A/m\(^2\) (again, nearly zero).

It is evident from the model results that for large load decrease, as may occur in an emergency-stop command, certain portions of the cell exhibit current reversal as seen in Figure 2. The reversed current condition lasts for approximately 330 seconds for the case studied. Further analysis of the model data shows that the main driver for this reverse current is the cell thermal non-uniformity. It is found that the air electrode exit portion of the cell results in a lower Nernst potential as compared to that at the inlet. Figure 2d shows the Nernst potential distribution on the cross-flow cell geometry immediately following the load decrease. The decreased Nernst voltage at the exit is due to the higher exit temperature (\(-100\) K higher), and this is enough to drive current in reverse.

Figure 3 illustrates the path of electric charge through the cell during the reverse current condition. The left portion of the cell in the figure shows positive current conditions which consume \(O_2\) and \(H_2\) and produce \(H_2O\) at the fuel electrode surface. The transferred electrons are provided to the right side of the fuel electrode where \(H_2O\) is reduced to generate \(O^-\) ions which travel in reverse through the electrolyte to generate \(O_2\) at the air electrode. The electrons released on the right side of the air electrode traverse back to the

Electrochemical Society Proceedings Volume 2005-07 859
left portion of the cell and the process continues until the thermodynamic driving potential no longer exists to drive this process.

The aforementioned cases all employed a 0.70 to 0.957 volt load change. The model was further implemented to determine the acceptable limit of load loss (now in terms of current) that would avoid the current reversal conditions. For the cross-flow, co-flow and counter-flow geometries, the limit of load current decrease was 83%, 85% and 86%, respectively, from their full load cell voltage condition of 0.70 volt. Load changes that would induce a greater decrease in cell load current will cause at least some portion of the cell to produce reversed current.

EXPERIMENTAL OBSERVATIONS

While extremely large load loss conditions can likely be avoided in normal fuel cell operation, they should still be considered a potential transient mode in the design of most fuel cell systems. The reverse current conditions that arise under such large load loss conditions, as identified by the model, have not been described previously, and it is important that further experimental work be performed to examine the conditions where such reversal occurs. If such conditions are indeed found to be possible for a given fuel cell system, then the SOFC system designer may need to consider their impact on the various cell components. For example, it is not yet clear if the thermodynamic potential that drives this current reversal will result in any new material degradation issues.

Addressing the latter issue of degradation can be readily accomplished using standard button cell testing methods. Since this is much easier to accomplish than the in situ measurement of current reversal in a stack, it is prudent to first determine if there are any concerns in operating a fuel cell in reverse prior to performing a detailed experimental validation for its existence. If new performance degradation mechanisms are identified due to operating an SOFC button cell in reverse, then expending additional effort to verify the occurrence of these reverse current operating conditions will be justified.

As such, we have performed experimental tests on an SOFC button cell whereby the current is forced in reverse. The SOFC button cells were purchased from the University of Utah, courtesy of Anil Virkar, and made using common SOFC materials; Ni, YSZ, and LSM. The cells were anode supported, and comprised of a 1 mm Ni-YSZ anode, a 25
µm Ni-YSZ interlayer, a 9 µm YSZ electrolyte, a 18 µm LSM-YSZ cathode interlayer, and a 50 µm LSM cathode. The cell active area was 2.19 cm². The basic test setup is shown in Figure 4. The cell was made to operate over a range of cell voltages while in 65% H₂+35%H₂O on the anode and 97% air and 3% H₂O on the cathode. The cell operating temperature was 800 deg. C.

A V-I curve of a cell is shown in Figure 5. The data was taken by initially conditioning the cell for approximately 3 hours at a constant voltage of 0.7 V, over which time the cell current increased to 1.2 A/cm². A V-I curve was then taken by increasing the cell voltage up to 1.42 volts. The cell was then put under a “stress load” of -0.9 A/cm² for only a short time (1.5 hours) to provide an accelerated durability study under reverse operation. After the stress loading, another V-I curve was obtained over the same cell voltage range. As can be seen, the cell has been slightly degraded in performance in both its fuel cell and electrolysis modes.

Additional cells of the same design were also tested under reverse current conditions and had similar degradation over time. As a first step in trying to identify the cause of the degradation, fractured cross sections of a cell run under reverse current conditions and a cell run only in normal fuel cell mode were examined using SEM and EDX analysis. Figure 6 compares the SEM images of a cell that had experienced reverse (negative) current operation for a period of about 5 hours to one that was run in normal mode (positive current). As can be seen from the SEM, the cathode of the cell that experienced reverse current has separated from the electrolyte over a significant length. This could be simply due to the process of fracturing the cell for SEM analysis, however we have not seen such results for numerous other cells run only in normal fuel cell mode. None of these latter cells have ever shown such delamination, hence it is not likely to have been caused by the fracturing.

![Figure 5. V-I curve for standard SOFC cell using 35% H₂O at the anode. The data denoted ‘after reversal’ is the data taken after operating the cell voltage under reverse current for 1.5 hours.](image_url)

EDX measurements on the same cells are shown in Figure 7. The vertical lines in the SEM images presented in Figure 6 show the path of the “line scan” EDX analysis. The striking result here is the measured increase in the amount of Ni within the electrolyte for the cell run in reverse mode. In addition, there is a build-up of Ni at the cathode side of the electrolyte. The cause for this is presently unclear, an further analysis is being done.
to confirm such a result. If the nickel can be electrochemically reduced under such conditions, then it may be possible for it to migrate across the electrolyte due to its electrochemical potential. This result would be surprising given that the most common oxidation state of nickel is +2—though +1 and 0 are also observed. The electron affinity of nickel is about -1.6eV at room temperature. Operation at 800 deg. C would likely change this only slightly. The results, however, suggest that these conditions provide enough nickel atoms at energy states where the observed ionization and migration can noticeably occur. Again, more studies will need to be performed to verify these initial results.

Figure 6. SEM of standard cell operated in positive current mode (left), and another in reverse current mode (right) for 5 hours. Both cell specimen micrographs shown were unpolished. Lower portion of the image shows the cathode with a less porous interlayer possibly cause by the deposition of nickel.

Figure 7. EDX scan results on unpolished cell specimens. Specimen having reverse current operation shows presence of nickel at the cathode, and an increase in nickel within the electrolyte.
CONCLUSIONS

This paper presents an investigation into the behavior of SOFC fuel cells during large load loss conditions (>80%). Such conditions have not received much attention, largely due to the focus of past (and current) research on achieving good steady state performance. Recent results from an application of a dynamic model to three planar geometries presently being considered by industry (co-flow, counter-flow and cross-flow) show the possible occurrence of reverse fuel cell operation (electrolysis) for sufficiently large load loss conditions. The reverse current exists over significant portions of the cell, starting from the moment of load perturbation up to the point where equilibrated conditions again provide positive current. Such reverse current conditions arise for all geometry types studied, although the cross-flow case is more severe for the same magnitude of load change. An estimate of the load change limit such that negative current conditions are avoided is 80% to 85%. Any load decrease greater than this will cause current reversal over at least portions of the cell. Initial experimental studies on SOFC button cells (Ni+YSZ/YSZ/LSM) show that reverse current conditions can cause performance degradation. While the direct cause for the degraded performance is not certain, the available SEM and EDX data suggest that nickel can transport across the electrolyte and deposit at the cathode interface and thereby weaken the cathode/electrolyte interface to the point of causing delamination.

These findings need to be considered preliminary. Measurements of spatial current density over a cell operated within a stack, having cell temperature variations typical of full-load conditions, need to be taken to validate the model results and the occurrence of current reversal under dynamic loads. The reverse current data shown in the present paper were taken using stress-load conditions to accelerate any degradation mechanism. More lengthy tests at reverse load conditions representative of what is likely to occur under typical cell operating conditions (e.g., -100 to -300 mA/cm²) need to be performed before reverse current operation at load loss can be identified as a mode that needs to be avoided in order to prevent unnecessary damage to the cell. In addition, more tests need to be performed to show the exact impact to the cell materials and verify the occurrence of nickel transport from anode to cathode as shown in the present EDX data.

REFERENCES

1. E. A. Liese, R. S. Gemmen, F. Jabbari, and J. Brouwer, Proceedings of the ASME Turbo Expo 1999, Indianapolis, Indiana, (1999).
2. M. D. Lukas, K. Y. Lee, and H. Ghezel-Ayagh, IEEE Transactions on Energy Conversion, PE-468-EC-0-01-1999, (1999).
3. P. Costamagna, L. Magistri, and A. F. Massardo, J. Power Sources, 96, 352 (2000).
4. S. Kimijima, and N. Kasagi, Proceedings of the ASME Turbo Expo 2002, June 3-6, Amsterdam, Netherlands, GT-2002-30111, (2002).
5. J. Padulles, G. W. Ault, J.R. McDonald, J. Power Sources, 86, 495 (2000).
6. E. Achenbach, J. Power Sources, 57, 105 (1995).
7. C. Haynes, J. Power Sources, 109, 365 (2002).
8. T. Ota, M. Koyama, C. Wen, K. Yamada, and H. Takahashi, J. Power Sources, 118, 430 (2003).
9. R. Gemmen and C. Johnson, C., to be published in J. Power Sources.
10. S. Ahmed, C. McPheeters, and R. Kumar, J. Electrochem. Soc., 138(9), 2712 (1991).
11. R. A. Roberts, J. Brouwer, R. S. Gemmen, and E. Liese, Proceedings of the ASME Turbo Expo 2003, Atlanta, Georgia, GT2003-38774, (2003).
12. W. A. Surdoval, S. C. Singhal, and G. L. McVay, in SOFC-VII, H. Yokokawa and S. C. Singhal, Editors, PV2001-16, p. 53, The Electrochemical Society Proceedings Series, Pennington, NJ, (2001).
13. R. S. Gemmen, E. Liese, J. G. Rivera, F. Jabbari, and J. Brouwer, Proceedings of the ASME Turbo Expo 2000, Munich, Germany, 2000-GT-0554 (2000).