INITIAL TESTING OF SOLUTIONS TO REDOX PROBLEMS WITH ANODE-SUPPORTED SOLID OXIDE FUEL CELLS

A. Wood\textsuperscript{a}, M. Pastoia\textsuperscript{a}, D. Waldbillig\textsuperscript{b}, D. Ivey\textsuperscript{b}
\textsuperscript{a} Versa Power Systems Ltd., 4852 52 St SE, Calgary, AB T2B 3R2, Canada
\textsuperscript{b} Department of Chemical and Materials Engineering
University of Alberta, Edmonton, AB T6G 2G6, Canada

ABSTRACT

The most commonly used solid oxide fuel cell (SOFC) anode material is a two phase nickel and yttria stabilized zirconia (Ni/YSZ) cermet. During typical fuel cell operation, this material remains a cermet; however, in a commercial SOFC system seal leakage, fuel supply interruption, or other situations may cause the anode to reoxidize. The cyclic reduction and oxidation (redox) of nickel will result in large bulk volume changes, which may have a significant effect on the integrity of interfaces within the fuel cell and thus may cause significant performance degradation. Following initial study of the degradation mechanisms and redox kinetics, a number of solutions have been devised. These can be broadly categorised into system solutions and unit cell or materials solutions. The former includes purge gas, other means to produce a reducing gas, cell reversal and passive solutions such as hydrides, oxygen getters and steam purging. The latter includes alternative anode materials, microstructural modification of anode functional layers (AFLs), graded porosity and composition of AFL and redox barrier layers. This paper discusses the pros and cons of each approach and some initial feasibility testing in short stack repeat units.

INTRODUCTION

Solid oxide fuel cells (SOFCs) are electrochemical devices that convert the chemical energy of a fuel into electrical energy with high efficiency. Several SOFC developers, including Versa Power Systems Ltd. (VPS), formerly Global Thermoelectric Inc., are currently developing anode-supported solid oxide fuel cells using a nickel and yttria stabilised zirconia (Ni-YSZ) cermet anode as the cell support (1,2,3). This type of SOFC is particularly suited to small-scale residential and industrial power generation (3-10 kWe) as defined in the US Department of Energy's Solid State Energy Conversion Alliance program (SECA). Cells are typically fabricated using nickel oxide and YSZ in the anode, and at the stack level, nickel oxide is reduced to nickel, with the associated volume change prior to operation. Unfortunately, nickel oxide reduction is completely reversible at typical SOFC operating temperatures depending on the oxygen partial pressure. If air is allowed to leak into the anode side of the fuel cell through seal leakage, fuel supply interruption, emergency stop or other events, then the nickel will oxidize to nickel oxide with the associated volume change. This reduction and oxidation process is termed redox cycling of the cell. Although nickel oxidation is completely reversible, it
has been found in practice that degradation of cell performance occurs, most likely due to mechanical damage from the volume changes on redox cycling (4).

Small-scale SOFC systems have very tight cost targets (<$800/kWe is the SECA phase 1 target) and so costly purge gas solutions to prevent cell oxidation are not feasible. As the oxidation of nickel is fully reversible, then it is the damage caused by this oxidation that must be prevented in order to achieve redox tolerance, and so there is the expectation that a technological solution can be found. This paper describes activities towards a commercially viable redox solution at VPS, including a review of the literature and patents related to redox tolerance of SOFCs. It is clear from the effort in this area that major SOFC developers believe there are several, potential cost-effective solutions to redox degradation that could be used depending on the specifics of the targeted market application and SOFC system.

MATERIAL AND STACK COMPONENT SOLUTIONS

The most elegant, and least expensive solutions are likely to be cell materials or component solutions. These are necessarily passive solutions requiring no special system power or control, and are therefore not likely to significantly impact system cost. A list of potential material/component solutions can be seen in table I. These have been subdivided into 3 headings:

1. materials (alternatives to Ni-YSZ cermet anodes);
2. microstructural modification (retaining the superior electrochemical performance of Ni-YSZ cermets with processing changes to minimise damage induced by volume changes associated with nickel redox); and
3. kinetic (utilising knowledge of reaction kinetics to slow the oxidation of nickel in critical areas of the cell so that a safe, practical system shutdown can be achieved).

Table I. Materials And Component Redox Solutions Broken Down Into Material, Microstructural Modification And Kinetic Concepts.

| Materials                        | Microstructural Modification                   | Kinetic/system                          |
|----------------------------------|------------------------------------------------|----------------------------------------|
| Alloy to replace nickel in cermet anode | Graded nickel content in anode functional layer (AFL) | Improved sealing (for gas containment) |
| Alternative, all-ceramic anodes   | Increased or graded porosity in AFL             | Oxidation barrier                      |
|                                  |                                                 | Lower operating temperature            |

It is entirely possible that materials solutions may not be able to eliminate all degradation due to oxidation of the cells, and to this end, the authors introduced the concept of redox
depth in a previous publication (5). Briefly, this is the amount of oxidation of the cell based on nickel content and assuming rapid oxidation kinetics such that all free oxygen reacts with nickel in the anode. System solutions could be used to prevent all oxidation, or else keep oxidation depth to a level that causes negligible degradation. The authors found in a previous publication (5) that this level is approximately 30% redox depth for VPS TSC-2 cells (i.e. 30% of the nickel in the cell by weight becoming oxidized). This level was also found to vary with modification of the microstructure, and so can be tailored to some extent.

**Alternative Anode Materials**

Redox degradation of SOFC cells is most easily resolved (in theory at least) by changing the anode materials from a cermet (typically Ni-YSZ) to an all-ceramic materials system. If the anode is oxide based and chemically stable, then it should not suffer large dimensional changes when moving between reducing and oxidizing environments as is the case when the electronic conductivity is provided by a metal. A number of compositions of materials have been studied to resolve both redox and sulphur tolerance problems, including doped strontium titanates (6) and doped lanthanum chromite (7,8). The key problems with these materials to date are the low electrochemical activity of the anode material, low electrical conductivity and high cost relative to a Ni-YSZ cermet. Another potential solution is to use an alloy (or even noble metal) with greater oxidation resistance (9), or else alloy the nickel with the aim of preventing sintering of fine nickel particles formed on redox cycling (10). This could lead to significant cell processing challenges.

**Modification of Microstructure**

Significant effort has been placed in the area of microstructural modification of the Ni-YSZ anode at VPS to improve cell redox tolerance. This is clearly the path that most developers have chosen to investigate based on the publications in this area (11,12,13,14). Lang et al (15) report complete redox tolerance for vacuum plasma sprayed cells. However, out of 10 references found in the technical literature using anode-supported cell architecture, none report multiple redox cycles with no degradation due to microstructural modification of a Ni-YSZ anode.

At VPS, previous work (4) has highlighted the key cause of redox degradation to be dimensional change of the anode functional layer (AFL) of the cell (see figure 1). The figure shows dimensional changes of coarse structured anode substrate and fine structured AFL Ni-YSZ cerments upon oxidation. The thick anode substrate has sufficient porosity that there is no measurable volume change on redox cycling, simply a density change of the substrate. However, the thinner AFL having higher density and finer nickel particle size shows significant volume change and tends to crack on redox cycling during thermomechanical analysis (TMA). Attempts to resolve this key cause of degradation are reported in detail by the authors in this volume (16). The main efforts centre around grading the composition and porosity of the AFL.
Figure 1. Reoxidation TMA of fine structured AFL sample (with the coarse structured anode substrate sample as a reference).

**Kinetic/System**

**Oxidation Barrier.** The authors have filed a provisional patent application relating to the use of a thin oxidation barrier layer (< 50 μm) used on the underside of the anode substrate of an SOFC, which, having a higher density, and using higher surface area nickel than the anode substrate slows the oxidation rate. When reduced, the layer is porous and testing has showed no diffusional limitation up to more than 1 A/cm², but upon oxidation the density of the layer increases significantly. The microstructure of such a cell can be seen in figure 2. Figure 3 shows the cumulative percentage voltage degradation at 60 A (0.74 A/cm²) against time with multiple redox cycles as indicated for standard VPS TSC-2 cells and cells using the oxidation barrier with varying weight percentage nickel oxide content of the layer. It can be seen that at 750°C, it takes almost 2 hours before the same degradation (equivalent to 30% redox depth) is reached with the oxidation barrier as with standard TSC-2 cells which take only 1 hour. This extra hour could allow significant system cooling to occur and thus prevent redox degradation.

Figure 2. Low magnification BSE SEM image of a fuel cell with an oxidation barrier.
Figure 3. Cumulative percentage voltage degradation at 60A (0.74 A/cm²) against redox time for standard TSC-2 cells and cells with oxidation barriers with varying nickel oxide content

**Improved Sealing.** A stack repeat unit test (single cell with stainless steel jigs and same current collection materials as used in the VPS stack) was performed using glass-ceramic seals to prevent leakage. The test was left for 15 hours at 750°C with no gas flowing at open circuit conditions and the anode inlet and outlet test pipes were closed outside the test furnace using standard ball valves. No degradation of power output was observed as seen in figure 4. Clearly a small system could be cooled within this timeframe and so high temperature check valves (see System Solutions) with reasonably gas tight sealing could prevent redox degradation. Note, that by the ideal gas law (PV=nRT), a sealed vessel cooled from 750°C to 20°C, produces a significant vacuum as P₁/T₁ ≈ P₂/T₂, and this needs to be accounted for in the system design.

Figure 4. Stack repeat unit test using glass-ceramic seal with gas flow stopped for 15 hours at 750°C and test station valves closed.
**Lower Stack Operating Temperature.** If cells can be produced with high power output operating at lower temperatures, then redox tolerance will be easier to achieve. The kinetics of nickel oxidation in an SOFC cell were reported by the authors in a previous paper (4). Based on this, cell tests with air introduced to the anode at various temperatures were carried out. The cells were oxidized for a pre-determined time with 120 ml/min air flow rate on a 10x10 cm cell. Figure 5 shows the cumulative percentage degradation plotted against redox depth with air introduced to the cell at various temperatures.

![Graph showing cumulative percentage degradation against redox depth with air introduced at various temperatures.](image)

**Figure 5.** Summary of the cumulative percent voltage degradation at 60 A (0.74 A/cm²) against oxidation time for cells redox cycled at various temperatures.

**SYSTEM SOLUTIONS**

The shutdown of anode-supported SOFC stack technology offers some unique challenges. The challenge is believed to be two-fold:

1) Redox limitations of current class of material systems with an anode-supported cell architecture.

2) Safety implications of anode / fuel processing gas, particularly hydrogen and carbon monoxide remaining in the fuel passageways. Hydrogen due to its flammability concerns, and carbon monoxide due to its flammability, toxicity, and its propensity to react with nickel at temperatures below 200 - 230°C to form nickel carbonyl which is also toxic and volatile.

Broad system engineering and material science thinking is required for technical success. For a holistic solution, one must think of normal and abnormal events that must both be safe and respect stack redox capabilities. Normal events would include the operation of
the SOFC cell/stack in a system including varying power outputs, start-up and shutdown. However, the range of unusual events are even more challenging. These include:

- System shutdown without fuel (power available on unit)
  - Loss of fuel

- Emergency stop of system (power not available on unit – “blind shutdown”), or similarly
  - Loss of control
  - True emergency stop
  - Loss of critical load power

At a high level, the stack needs to be robust enough to handle various situations at start-up/shutdown transitions to stack operating temperatures with fuel outages (that is no gas available for stack anode). Thus, the stack will be required to handle the likely ingress of oxygen. Due to the cell/stack material limitations, the redox ability of the stack should not be used as a normal part of any system start up and shutdown sequence. This technical consideration will minimize the likely number of redox cycles.

For redox, it is desired that a passive stack (or stack component) solution can be found. As in the case of a true “emergency stop of system”, no, or very limited electrical power may be allowed active on the system, including the system controller. In the case of “system shutdown without fuel”, cathode, or other airflows are likely available. It should also be assumed that cool downs during these failure conditions do not result in rapid cooldown due to the thermal mass of the stack and surrounding system compared with the low thermal mass of the gases passing through it.

In 2001, a number of solutions were proposed for improvements in Versa Power Systems prototype SOFC systems. System solutions were grouped into active, passive and dependent solutions and can be seen in table II. Active solutions require the use of electrical power, in addition to possibly control logic. Passive system solutions require no power or control logic. Dependent solutions are system add-ons or partial solutions that still require an active or passive solution to work, but enhance the redox tolerance. In addition, each solution may require various inputs and new components as described below. For the purposes of the discussion, a base SOFC system will be used to introduce the different designs, and a schematic is shown in figure 6.

In 2001, a number of solutions were proposed for improvements in Versa Power Systems prototype SOFC systems. System solutions were grouped into active, passive and dependent solutions and can be seen in table II. Active solutions require the use of electrical power, in addition to possibly control logic. Passive system solutions require no power or control logic. Dependent solutions are system add-ons or partial solutions that still require an active or passive solution to work, but enhance the redox tolerance. In addition, each solution may require various inputs and new components as described below. For the purposes of the discussion, a base SOFC system will be used to introduce the different designs, and a schematic is shown in figure 6.

![Figure 6. Schematic of a simplified SOFC system.](image-url)
Table II. Systems Redox Solutions Broken Down Into Active, Passive
And Dependent Concepts.

| Active                              | Passive                              | Dependent                              |
|-------------------------------------|--------------------------------------|----------------------------------------|
| Partial oxidation reformer          | Hydrides                             | Anode gas recirculation                |
| Alcohol-water mixtures              | Reversible oxygen getters / sacrificial material | Fuel enclosure (volume or piping)      |
| Thermal cracking of stored fuel source | Steam purge                          |                                        |
| Delayed purge of air or fuel        | High temperature check valves        |                                        |
| Activated carbon                   | Reducing gas cylinder                |                                        |
| Cell reversal                       |                                      |                                        |
| Water electrolysis                  |                                      |                                        |

Due to the length of the paper, only an introductory level discussion is supplied for each solution path. Internally, these concepts have been evaluated on a number of criteria including: effectiveness of solution, size, mass, cost, ease of implementation, efficiency, low fuel input requirement, low power input requirement, amount of additional system equipment, longevity, safety and technical risk for instance. When designing anode protection systems it is important to ensure that there are sufficient safety measures in place to prevent explosion, fire, or formation of hazardous nickel carbonyl in all failure modes. Many of the proposals within involve creation of flammable (H₂, CO, CH₄) and poisonous (CO) gases. Thus, appropriate engineering analysis and safety measures are required to implement any of these proposals. In addition, by introduction in this paper itself, it by no means deems each design proposal safe or recommended for use in SOFC systems.

**Active System Solutions**

**Partial Oxidation Reformer.** A partial oxidation or catalytic partial oxidation reformer can be used to generate a suitable reducing gas for anode protection. For this option, hardware would require an available fuel source (some fuel storage required), complete with fluid delivery systems for air and fuel, a reformer or burner zone, power source and simple control system (in addition to main controller). The partial oxidation reformer generates a gas mixture mainly comprised of nitrogen, hydrogen and carbon monoxide. The reformer could also be run at near stoichiometric conditions to produce a slightly reducing purge gas containing a greater amount of steam and carbon dioxide that is non-explosive and thermodynamically stable to prevent carbon formation if in contact with cool system components (17).

A variant of this proposal is described in a Siemens Westinghouse patent by Singh et al. (18) which uses a burner, or substoichiometric burner with an additional hydrogen storage supply capable of adding hydrogen as necessary to produce the desired ingoing cover gas.

**Alcohol-Water Mixtures Addition.** Having an “engineered” liquid fuel on-board the system is a suitable means to also produce a reducing gas for the anode as alcohols are...
one of the easiest fuels to reform. By having a suitable alcohol-water mixture, the following benefits result:

- Simple prevention of carbon formation
- Fuel composition adjustment to get desired purge gas
- Built-in freeze protection

This idea uses the thermal energy contained in the SOFC hot balance of plant to drive the endothermic reforming of the fuel. An additional reformer bed may be required for this design. A recent patent application by Halliop et al. (19) outlines a proposal using methanol in water to generate a purge gas in concentrations less than about 2.4% by weight and adds a flash evaporator for vaporization. In general, the purge could be flammable, however, the application favors a non-explosive mixture for safety considerations.

**Thermal Cracking of Stored Fuel Source.** A characteristic of the SOFC systems that can be used for hydrogen production is the high-grade heat. This is used with several of the anode protection methodologies listed herein. An additional methodology is to use a process referred to as thermal cracking. That is taking a hydrocarbon containing fuel, and deliberately cracking it into hydrogen gas and solid carbon \((C_nH_m \rightarrow nC + 0.5mH_2)\), likely using a carbon-forming catalyst such as nickel. Safety is a greater concern with this proposal as a pure hydrogen stream would be generated as a result.

**Delayed Purge of Air or Fuel.** Besides water, additional fluid streams available include air and fuel. For air to be available, this requires an air mover, power source and controls to be available. For fuel to be available, including the fuel outage scenario, a fuel reservoir is required in addition to appropriate valving and metering. Due to the likelihood of oxidation when adding air, and fuel cracking when adding fuel, this solution is more of a safety purge system, as opposed to a specific redox solution.

**Activated Carbon.** An activated carbon bed may suffice as an irreversible solution. This idea uses a carbon bed contained in the Hot BOP design (likely prior to the fuel processor). The carbon bed is maintained at a high temperature due heat transfer mechanisms from the hot BOP. In the case where reducing gas is required, air is passed through the hot carbon bed. The oxygen contained in the air reacts with carbon to generate a CO / CO₂ and nitrogen-rich stream, eliminating the free oxygen contained in air. Thus, reacting somewhat like a partial oxidation reformer, with the fuel source being the hot carbon contained in the system. As the reaction is exothermic, the reaction can be sustained on cooldown. It is conceivable that the carbon could be deposited in a dedicated component, ideally not the reformer due to deactivation of the catalyst. Safety is a significant concern with this proposal due to the amount of CO and nickel in the system.

**Cell Reversal by way of Applied Voltage or Current.** In SOFC at high temperature and open circuit conditions, the cell voltage is directly related to the gas composition in the anode and cathode (air) through the Nemst potential. Thus, if an external voltage is applied to a cell or stack, it is expected that the flow of oxygen ions can be reversed (flowing anode to cathode) to maintain the anode at a safe oxygen partial pressure. This concept is as outlined by Prediger et al. and Mukerjee et al. (20,21).
Water Electrolysis. If water and power are available on the system, a “mini” electrolyzer could be used to generate a relatively pure hydrogen stream that could be used to create suitable reducing gas for the SOFC anode. Cost, complexity and safety are some of issues to address with this solution.

Passive System Solutions

Hydrides. Metal hydrides literally trap hydrogen within an alloy, much like a sponge absorbs water. When heat is applied, the gas is released. “High temperature” reversible hydrides such as magnesium hydride (MgH₂) are typically used at 300°C. At 650-700°C and near atmospheric pressure, would a material with similar properties have an ability to store and release a small amount of hydrogen to maintain a reducing atmosphere for the SOFC stack? A more detailed investigation would be required to identify materials that are suitable for this unique SOFC application. The high enthalpies of formation (endothermic) seen in today’s “high temperature” hydrides would likely not be a significant issue for SOFC systems containing MJ of internal energy at high temperature. Details in patents by Mukerjee et al. (21), and in more detail by Singh et al. (18) give insights into some candidate materials.

Reversible Oxygen Getters / Sacrificial Material. In SOFCs, it is possible to use relatively unstable materials, such as nickel in various forms, to chemically react with any free oxygen that enters into the anode vicinity at high temperature. The oxygen getter reacts as needed to maintain the anode oxygen partial pressure at a suitably low value as described previously. The oxygen getter could be installed in the piping to and from the stack, in the stack itself, or even in the anode material if properly engineered. The oxygen getter material is readily re-reduced back to metallic form on the reintroduction of reformate. Recent Delphi patent submissions (22,23) provide some additional details.

Steam Purge, Including Delayed Purge. Assuming that liquid water is available (on system or through facilities), water can be added to the system and vaporized by the thermal energy contained in the hot balance of plant. Assuming that a nickel-containing reformer is in series with the SOFC anode cavity, the reformer can be used to set up a slightly reducing gas by way of oxidizing some of the reforming catalyst ($H_2O(q) + Ni(s) \rightarrow NiO(s) + H_2(g)$).

As an alternate to the reformer, if redox of the reformer is not desired, an additional, likely nickel containing bed can be used. If beneficial to the SOFC stacks, the steam purge may be delayed for a period of time until the stack is at a lower temperature.

Some preliminary testing has been carried out at VPS using nitrogen with 80% steam to simulate steam purges in stack repeat unit tests. Power curves to 60 A on 10x10 cm cells (0.74 A/cm²) were run before and after steam purges for various lengths of time, and the cumulative percentage voltage degradation at this condition is plotted against steam purge time in figure 7. For reference an equivalent test using air instead of steam is plotted on the same axis. It is clear that the simulated steam purge shows less degradation for a given purge time.
Figure 7. Comparison of cumulative percentage voltage degradation after steam purge and air purge for equivalent times at 750°C.

Another set of tests were performed whereby stack repeat units were subjected to a simulated steam purge during a 30 hour cooldown (a worst case for a small SOFC system) from 750°C to 300°C. As a reference thermal cycles without steam purge were run at the start and end of the test. Figure 8 shows the cumulative percentage voltage degradation with each cycle at 0.74 A/cm² and 750°C. It should be noted that the purge is not run through a reformer or other metal before entering the anode, so is more oxidizing than anticipated in the final system version of this concept. The authors have filed a provisional patent application for this concept.

Figure 8. Cumulative percentage voltage degradation at 0.74 A/cm² after steam cooldown and thermal cycles for 2 stack repeat unit tests.
High Temperature Check Valves (gas containment). Of the passageways for free oxygen to enter the SOFC stack, the anode in and anode out ports are two of the most likely. Thus, if a low-cost and effective high temperature check valve could be developed, it could be used to meet the anode protection needs of the stack providing oxygen ingress by other means is low. With this design, upon system shutdown, the valves would close, thus closing in the anode atmosphere (24). A variant of this may use an additional gas supplied to the stacks to create a positive pressure environment within the stacks further to prevent ingress of free oxygen. The additional gas would also assist in maintaining the anode cavity pressure.

Small Reducing Gas Cylinder. A relatively simple solution is the extension of today's most commonly used anode protection method. Using a small, high pressure cylinder of gas (say <1 m³ of gas / kW SOFC stack) and fail open solenoids providing a low flow rate of gas may be economic in some situations depending on the robustness of the SOFC anode and flow rates required.

Other Features – Dependent Solutions

Anode Gas Recirculation. Adding a component such as a warm fuel recycle blower can be useful in that the anode gas can continually be circulated in and out of the SOFC anode chamber.

Fuel Enclosure. Another design feature possibly useful to maintain a reducing atmosphere is to either increase the amount of fuel volume contained in the stack or system, or to control the environment around the anodes where oxygen may enter the anode cavity. A variety of mechanical designs could be used to implement this proposal.

CONCLUSIONS

Solid oxide fuel cells (SOFCs) offer many advantages over low temperature fuel cells for small-scale power generation systems (3-10 kWe) due to the potential for internal reforming of realistic hydrocarbon fuels which greatly simplifies the system, lowers costs and increases efficiency. Versa Power Systems Ltd. (VPS) is actively developing anode-supported SOFC systems using a nickel and yttria-stabilised zirconia cermet anode as the cell support. A key challenge to the commercialization of anode-supported SOFCs is redox degradation. This is the damage caused by volume changes in the cell when nickel in the anode is repeatedly oxidized and reduced during system operation in a commercial application.

The search for solutions to redox degradation has become an active area of fuel cell research in the last 5 years, as can be seen from more than 20 US patents and patent applications found by the authors in this time period. VPS has submitted 4 patent applications in this area and conducted a great deal of research and development towards a commercially viable solution.

By applying materials science and systems engineering concepts, several potential solutions have been identified and preliminary testing has been conducted to establish feasibility. These solutions are summarized in tables I and II. It is likely that a
combination of approaches will be used in the first commercial systems and the details of the solution will be application specific, depending on such factors as indoor or outdoor operation, available services and likely reliability of the services.

At this stage VPS has demonstrated the feasibility of a number of solutions to redox degradation and further technical and economic analysis will determine which will be implemented in system prototypes.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the support of Versa Power Systems Ltd., University of Alberta and COURSE for providing funding for the testing work. In addition, the authors would like to thank Xinge Zhang, Tahir Joia, Dale Steedman and Murray Tilleman for experimental assistance.

REFERENCES

1. B. Borglum, E. Tang, D. Prediger, M. Pastula, *these proceedings*.
2. N. Christiansen, S. Kristensen, H. Holm-Larsen, P. H. Larsen, M. Mogensen, P. V. Hendriksen, S. Linderoth, in *Sixth European Solid Oxide Fuel Cell Forum Proceedings*, M. Mogensen, Editor, p. 20, European Fuel Cell Forum, Oberrohrdorf, Switzerland, (2004).
3. F. Tietz, in *Sixth European Solid Oxide Fuel Cell Forum Proceedings*, M. Mogensen, Editor, p.289, European Fuel Cell Forum, Oberrohrdorf, Switzerland, (2004).
4. D. Waldbillig, A. Wood, D. Ivey, *Solid State Ionics*, accepted for publication (2005).
5. D. Waldbillig, A. Wood, D. Ivey, *J. Power Sources*, accepted for publication (2005).
6. S. Hui, A. Petric, *J. Eur. Ceram. Soc.*, 22, 1673 (2002).
7. S. Tao, J. T. S. Irvine, *J. Electrochem. Soc.*, 151, 2, A252 (2004).
8. S. Tao, J. T. S. Irvine, in *Sixth European Solid Oxide Fuel Cell Forum Proceedings*, M. Mogensen, Editor, p.1417, European Fuel Cell Forum, Oberrohrdorf, Switzerland, (2004).
9. P. Huang, E. Tang, D. Ghosh, US Patent Application No. 0098406 A1 (2002).
10. D. Waldbillig, A. He, D. Ivey, in *Towards a Greener World, Conference Proceedings*, Hydrogen and Fuel Cells Conference and Trade Show, p. 174, Vancouver, Canada, (2003).
11. D. Fouquet, A.C. Muller, A. Weber, E. Ivers-Tiffee, *Ionics*, 8, 103-108 (2003).
12. G. Robert, A. Kaiser, E. Batawi, in *Sixth European Solid Oxide Fuel Cell Forum Proceedings*, M. Mogensen, Editor, p.193, European Fuel Cell Forum, Oberrohrdorf, Switzerland, (2004).
13. P. Holtappels, C. Sorof, M. Verbraeken, S. Rambert, U. Vogt, *ibid*, 201 (2004).
14. A. C. Muller, D. Herbstritt, E. Ivers-Tiffe, *Solid State Ionics*, **152-153**, 537-542 (2002).

15. M. Lang, T. Franco, M. Johnson, G. Schiller, P. Szabo, in *Sixth European Solid Oxide Fuel Cell Forum Proceedings*, M. Mogensen, Editor, p. 877, European Fuel Cell Forum, Oberrohrdorf, Switzerland, (2004).

16. D. Waldbiliag, A. Wood, D. Ivey, *these proceedings*.

17. M. Pastula, J. Devitt, R. Boersma and D. Ghosh, in *SOFC VII*, H. Yokokawa and S. C. Singhal, Editors, *PV2001-16*, p. 180, The Electrochemical Society Proceedings Series, Pennington, NJ, (2001).

18. P. Singh, R. A. George, US Patent No. 5,928,805, (1999).

19. W. Halliop, G. M. McAlary, R. A. George, US Patent Application No. 20040106019, (2004).

20. D. Prediger, D. Ghosh, US Patent Application No. 20020028362, (2002).

21. S. Mukerjee, M. J. Griev, K. Keegan, US Patent No. 6,620,535, (2003).

22. K. J. Haltiner, S. Mukerjee, D. M. England, M. T. Faville, S. M. Kelly, B. Edlinger, J. Tachtler, US Patent No. 6,744,235, (2004).

23. D. M. England, K. J. Haltiner, S. M. Kelly, M. T. Faville, US Patent Application No. 20030235752, (2003).

24. H. R. Mieney, K. J. Haltiner, US Patent No. 6,680,136, (2004).