DESIGN AND PERFORMANCE OF TUBULAR SOLID OXIDE FUEL CELLS

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ABSTRACT

Single solid oxide fuel cells which, when series-parallel interconnected, combine to form multi-kW modules, are examined in detail to quantify processes affecting available running power. These processes involve power losses across internal resistances, most of which are accounted for by the geometry and known resistivities of the materials employed. Other major power losses are due to diffusion of gases through the electrodes and porous support tube of the cell. The experimental methods employed to determine these quantities are described, along with examples describing the effect of temperature and of current density.

BACKGROUND

High-temperature solid oxide electrolyte cells are the product of much theoretical and experimental work extending from 1900, when Nernst (1) observed the electrolytic evolution of oxygen from a rod of (ZrO$_2$)$_{0.86}$(Y$_2$O$_3$)$_{0.18}$. Solid electrolytes were studied in oxygen concentration cells by Haber and Moser (2) in 1905.

The transference number of the oxygen ion in (ZrO$_2$)$_{0.86}$(CaO)$_{0.15}$ electrolyte is near unity as demonstrated by Kingery, et al. (3). The same electrolyte was used in a cell by Weissbart and Ruka (4) to measure near-theoretical voltages for the hydrogen-oxygen reaction. Archer (5), et al., constructed multi-cell batteries using stabilized zirconia electrolyte and platinum electrodes.

The electrolyte employed by Archer was in a self-supported "bell-and-spigot" geometry. To decrease internal resistance as much as possible, the active cell region of the electrolyte was machined to a minimum practical thickness of approximately 400μ. The machined electrolyte was a comparatively thick structure, wasteful of power due to excessive voltage drop across the large internal resistance.
Electrolyte having considerably less thickness was needed to decrease internal resistance and also to minimize the cost of dense zirconia, particularly where yttria rather than calcia is the stabilizing agent. Isenberg, et al. (6) evaluated a cell with an approximately 30μ thick zirconia-yttria electrolyte, formed by chemical vapor deposition (CVD); which developed near-theoretical open-circuit voltage.

Isenberg (7) also evaluated a 7-cell, series-interconnected unit with 12 cm² active cell area. The 40μ thick air electrode was a composite oxide type with porous and partially electronically conducting stabilized zirconia backed by a CVD tin-doped indium oxide current collector. A 30μ electrochemically vapor deposited (EVD) yttria-stabilized zirconia electrolyte and a 30μ sintered cobalt-zirconia cermet completed the cell structure. Interconnection of cells was accomplished with EVD-deposited, magnesium-doped lanthanum chromite. Support for the cells in this design was provided by a porous, calcia-stabilized zirconia tube on the inner (fuel electrode) surface of the 7-cell unit. Such cells were capable of operation at an average power density of 0.24 W/cm²-electrode area at 1000°C. More than 5000h of operation was achieved with the 7-cell stack using simulated coal gas as fuel. With this data base, the high-temperature solid oxide fuel cell design was then developed into the present type, which is envisioned as best for electrical generator configurations.

This paper describes one part of a multi-phase program to pursue the high-temperature SOFC (Solid Oxide Fuel Cell) technology toward its use in the commercial generation of electrical power. The objective is to establish baseline performance capability under a variety of test conditions for specific sources of fuel such as natural gas. The technology is based on materials, processes and designs developed for technical and economic feasibility.

EXPERIMENTAL

The new cell structure and method of cell interconnection, according to Isenberg (8), is as follows:

The tubular, single-cell design employs a strontium-modified lanthanum manganite cathode, an yttria-stabilized zirconia electrolyte and a nickel cermet anode (Figure 1). The cell component layers are supported on a porous, calcia-stabilized zirconia tube. The anode (outermost layer) of the cell is contacted directly by nickel felt. The cathode (innermost layer) of the cell is contacted by a sealed interconnection (IC) material, which is stable both in oxygen and in fuel/H₂O gas mixtures. The IC then contacts nickel felt on the exterior surface of the cell. The design thus establishes both cathodic and anodic electrical terminals in the fuel (reducing) atmosphere.
The experimental apparatus is shown schematically in Figure 2. It comprises an alumina muffle tube which contains the test cell in such a way that fuel gas flows upward over the cell exterior while air is admitted to the cell interior. The air is pre-heated within an alumina air feed tube; initially contacts the cell air electrode at the closed, or lower end; then reverses direction and flows toward the open end, where partially spent air and partially spent fuel mix and combust. Typical cell operation is at 85% fuel utilization and 25% air utilization, followed by direct combustion of the remaining gases. The fuel cell produces both electrical and thermal energy.

The apparatus employs nickel bus bars for current leads to a controlled-resistance external load. Platinum leads measure cell potentials directly at the cell anode and cathode. The muffle tube housing is contained within a 3-zone furnace. Cell temperatures are measured within the air chamber with a Pt, Pt, 10% Rh thermocouple. Control over the fuel/H₂O ratio fed to the cell is accomplished by bubbling hydrogen through water which is thermostatically controlled at a temperature corresponding to the desired water partial pressure.

Mixtures of fuel and H₂O are admitted to the cell (anode) at flow rates designed to keep fuel utilization at a constant value, e.g. 85%, during changes in cell operating current. Similarly, air flow matches any cell current to provide for constant air utilization, e.g., 25%.

Experimental values of total cell resistance, R, were obtained by measurement of the virtually instantaneous voltage drop observed by oscilloscope upon interruption of a known current through the cell. These experimental values are in reasonable agreement with calculation based upon the dimensions of the cell, the known resistivity of the electrolyte, and estimates of electrode resistivities.

Since cell construction employs nickel bus bars comprising an equipotential along the entire length of the cell, the working cell voltage, Vₜ, is constant along the length of the cell, even though fuel/H₂O ratios vary. When current passes through the cell, the terminal voltage is given by:

\[ Vₜ = E - IR - η₁ \]  

where  
Vₜ = the working voltage of the cell, volts.  
E = the reversible voltage of the cell, volts.  
I = the current passing through the cell, amps.  
R = the electrical resistance of electrodes and electrolyte, and contacts, ohms.  
η₁ = the polarization voltage losses associated with irreversibilities in electrode processes, volts.
In general, $E$, $I$ and $\eta_1$ are nonlinear functions of position along the length of the cell. These parameters are subject to the condition that their sum, at any specific set of operating conditions is equal to, $V_T$, as in Equation [1]. Thus, each are some mean or weighted average of their local values.

Total voltage losses at the cathode are basically derived by comparison of loaded cell voltage for the cathode in air vs. the cathode in pure oxygen. Within this total cathodic voltage loss, $\eta_d$, that portion due to $N_2-O_2$ counter diffusion in macro pores, is estimated by measurement of the difference of loaded cell voltages in air versus He - 21% $O_2$. The difference between total cathodic voltage loss, and $\eta_d$ is attributed mainly to Knudsen flow in very fine capillaries and is labelled $\eta_x$.

Anodic voltage losses, $\eta_f$, are estimated by reference to a performance model for the fuel electrode. The model estimates that the observed voltage loss when the fuel gas is diluted with nitrogen, 1:1, volumetrically, is approximately equal to fuel electrode $H_2-H_2O$ counterdiffusion losses in macro pores.

Values of IR-free voltage losses were plotted by adding the applicable IR value to data for the terminal voltage, $V_T$, versus current, $I$. $\eta_d$, $\eta_x$ and $\eta_f$ are similarly added to generate cumulative $\eta_d$-free, $\eta_x$-free and $\eta_f$-free curves which illustrate the individual contributions of each of these voltage-loss components as a function of current density.

RESULTS AND DISCUSSION

Upon connecting the cells to an external load, reproducible $V-I$ curves are obtained. Figure 3, the case of 850°C operation up to 450 mA/cm$^2$, shows that virtually all of the voltage drop at 150 mA/cm$^2$ is due to IR (ohmic) voltage losses. At 450 mA/cm$^2$, diffusion losses, $\eta_d$, $\eta_x$, $\eta_f$ have greatly increased, and constitute approximately 50% of the total voltage drop. The topmost curve represents idealised operation with zero voltage loss. Other activated processes, such as charge transfer, comprise negligible contributions to cell power losses.

Figure 4, the case of 1025°C operation up to 450 mA/cm$^2$, shows a similar, decreasing voltage loss due to diffusion effects except that, at 450 mA/cm$^2$, diffusion-type losses account for only approximately 30%, with $\eta_x$-type losses virtually absent. In general, diffusion voltage losses decrease rapidly with increasing temperature so that fuel cell operation is most efficient at higher temperatures.
Cell performance stability is illustrated by output voltage, under constant running parameters, over a period of time. Figure 5 illustrates the loaded voltage of a cell as a function of time at 950°C, 250 mA/cm², 85% H₂ fuel utilization and 25% air utilization. Another aspect of performance stability is the voltage drop due to electrical resistance of the cell. As previously mentioned, IR drop constitutes the major voltage loss in the cell over current densities of practical interest. Figure 5 also shows resistance levels for this test cell during time on test.

SUMMARY

The results of the high temperature cell tests have provided insights with respect to specific voltage losses, and performance stability for tubular solid oxide fuel cell. \( V_T \), the working cell voltage, is affected by four voltage loss components. IR, the material/geometry-based voltage loss due to resistance, constitutes the major inefficiency over current densities of interest. The electrical resistance of the cell is the sum of its parts, metallic and semiconducting. The overall result of increasing operating temperature is to lower cell resistance moderately, resulting in a second-order effect on overall performance, compared to diffusion mechanisms.

Cathode voltage losses derive from \( N_2-O_2 \) counterdiffusion through the pores of the cathode structure and also through the porous support tube. Another, lesser cathodic loss is measured which is attributed to Knudsen flow of \( N_2-O_2 \) through very small capillaries or grain boundaries.

Anode voltage losses due to counter diffusion of \( H_2-H_2O \) are minor and play less of a role in affecting fuel cell performance. In all cases of diffusion limitation, however, increasing operating temperature helps to lower voltage losses and increase performance.

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Fig. 1 - Tubular fuel cell in cross-section.

Fig. 2 - Fuel cell test stand schematic.
Fig. 3 - The influence of $\eta_{IR}$, $\eta_d$, $\eta_x$, and $\eta_f$ on tubular fuel cell performance at 950°C, 85% H$_2$ fuel utilization and 25% air utilization.

Fig. 4 - The influence of $\eta_{IR}$, $\eta_d$, $\eta_x$, and $\eta_f$ on tubular fuel cell performance at 1025°C, 85% H$_2$ fuel utilization and 25% air utilization.
Fig. 5 - Fuel cell voltage versus time on test at 950°C, 250 mA/cm², 85% H₂ fuel utilization and 25% air utilization.