

Fabrication and Operational Experiences of a 6 kW Molten Carbonate Fuel Cell Stack

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Abstract—An MCFC stack consisting of 20 unit cells with an effective electrode area of 3,000 cm² was prepared and operated to verify the performance and reliability of the cells. All the porous cell components such as anode, cathode and matrix including electrolyte sheets were manufactured by the tape casting method. Hard-rail type separator made with AISI 316 L stainless steel was used for separating fuel and oxidant gases and conducting electricity between unit cells as well. When fuel gas (H₂ : CO₂ : H₂O = 72 : 18 : 10) and oxidant gas (Air : CO₂ = 70 : 30) were supplied at a flow rate of 40% utilization to the stack at 650 °C, the output power of the stack was measured as 7.6 kW at its peak time. This was much higher than the design value of 6 kW. In addition to this high performance, the standard deviation of cell voltage among 20 unit cells was a mere 3 mV. The stack showed little performance decay up to 1,800 hours of operation time. After an unexpected thermal cycle due to the failure of the pre-heater for fuel gas around 2,000 hours, however, the decay rate became larger accordingly with operating time. The total operation time reached 5,600 hours including 4,800 hours under load in which a total of 23,202 kWh was generated. The evaluation of the stack was quite satisfactory in general except for the difficulty in temperature control under full load.

Key words: MCFC, Stack Operation, Cell Performance, Polarization, Endurance

INTRODUCTION

The molten carbonate fuel cell (MCFC) has a tremendous future in the electric power generation market because of its outstanding characteristics. These include high thermal efficiency, low environmental intrusion, fuel flexibility, modular design, co-generation capability [Bloemen and Mugerwa, 1993].

Recognizing this high potential, the Korean government in association with KEPCO, SHI, KIST and six universities launched an MCFC development program in 1993 aimed at construction of a 100 kW demonstration plant by 2002. The first phase of this program, of which the goal was to establish the fundamental technologies by 1996 through manufacturing a 2 kW stack with a lifetime of longer than 2,000 hours, has been successfully completed. The second phase of the program from 1997 to 2002 is divided into two sub-phases: 1) development of a 25 kW system by 1999 and 2) construction of a 100 kW demonstration plant by 2002. As an interim target before the 25 kW system, a 6 kW stack was operated to verify scale-up technology. For the next step toward the commercialization of the MCFC power plant, a 250-300 kW module unit which includes reformer, heat recovery steam generator and DC-AC inverter in one unit will be developed by 2005 followed by several field tests to disseminate the technology in various applications. In addition to the system development

for proof-of-concept, the improvement of the technology itself for longer lifetime and higher reliability is intensively and extensively pursued in this program. This activity extends from further optimization of the current technology to a survey of new materials for cell components [Hong et al., 1997].

In this paper, the experience with the 6 kW stack operation and part of the results from single cell operation for performance analysis will be presented to provide an overall view of Korea's R & D status in MCFC technology.

PREPARATION OF STACK

1. Cell Components

For the fabrication of all the cell components, tape casting method has been employed. The fabrication technology has been continuously improved to get better cell performance, higher production yield and scale-up of size as well. This was done by the optimization of the process variables that include slurry composition, ball milling condition, tape casting condition and sintering condition [Oh et al., 1997]. The optimized specification of each component required for state-of-the-art cell performance is summarized in Table 1. However, the current cell components still demand more research effort to achieve the goal of commercialization that can be represented by 40,000-hour of lifetime. New materials such as Ni-Al alloy anode, MgO-stabilized cathode, Li/Na electrolyte, etc., are expected to or have already begun to replace the old ones.

2. Separator (bipolar plate)

The separator has dual functions: gas separation between anode and cathode, and electrical interconnection between unit cells. It

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Table 1. Specifications of cell components

| Component | Composition/Physical properties | |
|-------------|---------------------------------|-------------------------------|
| Anode | • Material | Ni-10% Cr |
| | • Pore size | 3-4 μm |
| | • Porosity | 50-60% |
| | • Thickness | 0.6-0.8 mm |
| | • BET area | 0.1-0.2 m^2/g |
| Cathode | • Material | NiO |
| | • Pore size | 8-10 μm |
| | • Porosity | 70-80% |
| | • Thickness | 0.5-0.7 mm |
| | • BET area | 0.3-0.4 m^2/g |
| Matrix | • Material | $\gamma\text{-LiAlO}_2$ |
| | • Pore size | 0.3-0.4 μm |
| | • Porosity | 55-65% |
| | • Thickness | 0.3-0.5 mm |
| | • BET area | 8-9 m^2/g |
| Electrolyte | • Material | 62Li-38 K carbonate |

is usually made with AISI 316 L or 310 S stainless to withstand the corrosive conditions imposed by high temperature and molten carbonate. However, certain parts of the separator require further protection: for example, Al coating on wet seal area and Ni coating on anode gas channel.

Another important issue is the design of the internal manifold and gas channel of unit cell. Not only uniform gas distribution but also cooling capacity by cathode-side gas flow fully depends on how good the design is. Anode and cathode gases flowed in a co-flow direction and the gas flow pattern inside the 6 kW stack was a reverse U-configuration. Two mask plates and one center plate which has gas channels on both sides formed by etching were laser-welded together to make a separator. Hard-rail type separators, which were used for the 6 kW stack, will be replaced by soft-rail type for the 25 kW stack, which is expected to have a longer lifetime. To get the temperature profile inside the stack a thick temperature plate equipped with nine thermocouples was inserted in every five unit cells.

After the assembly, the stack underwent pretreatment according to a pre-determined schedule. During this period, organics in matrix and electrolyte sheets were burnt out and carbonates were melted down around 500 °C followed by cathode oxidation and lithiation in situ. When stack temperature reached 650 °C, reactant gases were supplied for the operation. And the time to start supplying reactant gases was regarded as the beginning of operating time.

OPERATION RESULTS

1. Single Cell Operation

The thermodynamic reversible potential (E°) of a fuel cell can be calculated by Nernst equation at a given operating condition. When current flows, however, the cell voltage (E) will be decreased from its reversible potential because of irreversible losses: ohmic polarization (IR , internal resistance), electrode polarization at both electrodes (η_a and η_c) including activation and concentration polarization. In addition to them, a practical cell has another

Table 2. Set-up variables & operating variable effect

| Set-up variable | Optimized value | Operating variable | Effect of change |
|----------------------|-----------------------------|--------------------|---|
| Holding pressure | 2-3 kg/cm^2 | Temp. | +1.54 mV/K |
| Electrode protrusion | +50 μm | Utilization | H ₂ -1.7 mV/% Air -0.5 mV/% |
| Electrolyte filling | 160% of total porosity | Oxygen gain | 90 mV |
| Porosity | Ano. +50% Cat. +60% | Pressure | 75 logP (atm) |

source of voltage drop, so-called Nernst Loss (NL) due to inevitable gas concentration gradient across the electrode when electrochemical reactions take place. Thus, the voltage of a practical cell under operation can be expressed by the following Eq. (1) [Bockris and Srinivasan, 1969].

$$E = E^\circ - \eta_a - \eta_c - IR - NL \quad (1)$$

The goal of R&D of MCFC is to minimize the polarization so that E approaches E° . This can be done either by modification of operating conditions, i.e., higher pressure and temperature, gas composition change, or by improvement of components' structures, more conductive electrolytes, *etc.* However, trade-offs exist between higher performance and problems associated with durability of cells encountered at the more severe conditions [Hirschenhofer et al., 1994].

The first thing to do for minimization of polarization is to optimize the set-up variables such as holding pressure, electrolyte filling level, *etc.* This has been already finished through many single cell operations and the results are summarized in Table 2. The state-of-the-art single cell voltage measured at this optimized condition is about 0.83 V at the current density of 150 mA/cm^2 .

Once the contribution, particularly as a function of operating time, to total polarization from each source is identified, the order of priority in developing countermeasures to extend lifetime can be established. For the measurement of internal resistance, a milliohm meter (HP model: 4338A) which utilizes AC impedance method at 1 kHz was used. For the measurement of NL, an experimental method is generally applied as shown in Fig. 1. The difference between OCV (open circuit voltage) and an extrapolated voltage from a linear I-V line obtained when the utilization of fuel or oxidant gas is fixed accordingly to the load, is defined as NL. Typical values of internal resistance and NL at 40% fuel utilization for 10 cm×10 cm single cell with state-of-the-art performance are 2.8 $\text{m}\Omega$ and 80 mV, respectively.

After the IR and NL were measured, a special single cell which has the reference electrode attached to the cathode side was operated to distinguish η_a and η_c from total polarization. The reference electrode, only one available at 650 °C, consisted of a gold wire and double alumina tubes. The external tube had a tiny hole of 3 μm in diameter to form a salt bridge. The gas composition which flowed through the reference electrode was identical with that of the cathode side. Fig. 2 shows the individual changes of η_a and η_c as well as of total polarization with operating time up to 3,000 hours. As clearly depicted in Fig. 2, cathode polarization

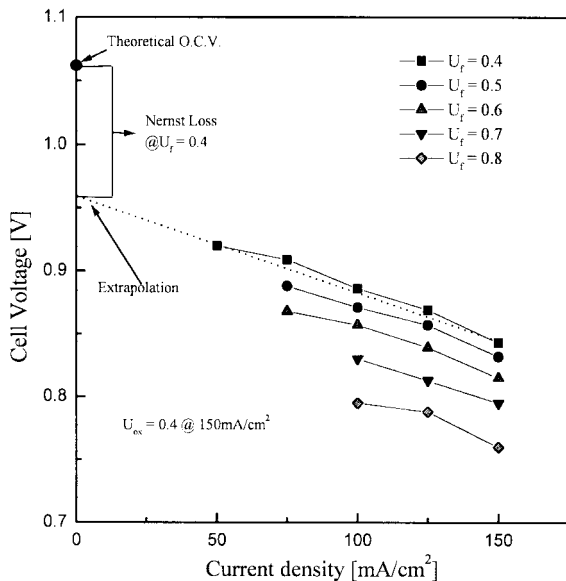


Fig. 1. Measurement of Nernst Loss in an MCFC single cell.

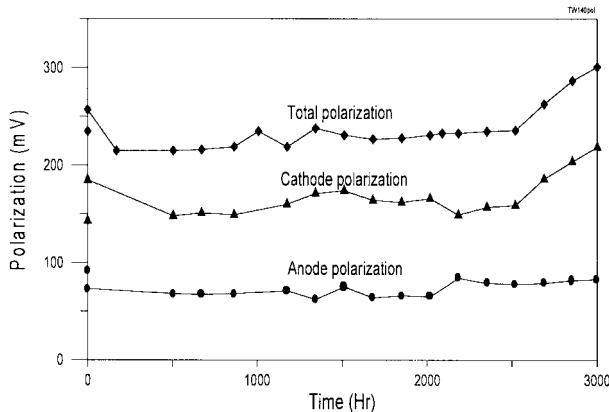


Fig. 2. Polarization change of a single cell with operating time.

not only makes a major contribution to total polarization but also assumes almost all responsibility for the increase in total polarization at the end of the operation. The former is attributed to the sluggish reaction and the lower conductivity of cathode. The latter is due to the microstructure change of cathode by NiO dissolution. Stabilized cathode by either addition of MgO or coating with LiCoO_2 could be a solution to this problem.

2. 6 kW Stack Operation

A 6 kW-class stack assembled with cell components in Table 1 and the separators mentioned above were operated for 5,600 hours as a preliminary test for the 25 kW stack scheduled to operate in October 1999. When a stack is evaluated, three major points are generally involved: 1) initial performance, 2) voltage distribution among unit cells, and 3) endurance and decay rate. The operation result of the 6 kW stack will be explained, compared with its design requirements in Table 3.

2-1. Initial Performance

Fig. 3 shows the I-V curve and output power of the stack at the operating conditions described in Table 3 after 40 hours from reaching 650 °C. The OCV and the stack voltage at 150 mA/cm² were measured as 21.81 V (1.09 V/cell) and 15.92 V (0.79 V/cell),

Table 3. Design requirements of 6 kW stack

| Item | Target |
|--------------------------|--|
| Output power | 6 kW |
| Effective electrode area | 3000 cm ² /cell |
| No. of unit cells | 20 |
| Manifold | Internal |
| Performance | 0.7 V at 150 mA/cm ² |
| Lifetime | 2,000 h (<1%/1,000 h) |
| Operating Temp. | 650 °C |
| condition Pressure | 1 atm |
| Utilization | Anode 40-60% |
| | Cathode 40% or less |
| Gases | Anode H ₂ : CO ₂ : H ₂ O=72 : 18 : 10 |
| | Cathode Air : CO ₂ =70 : 30 |

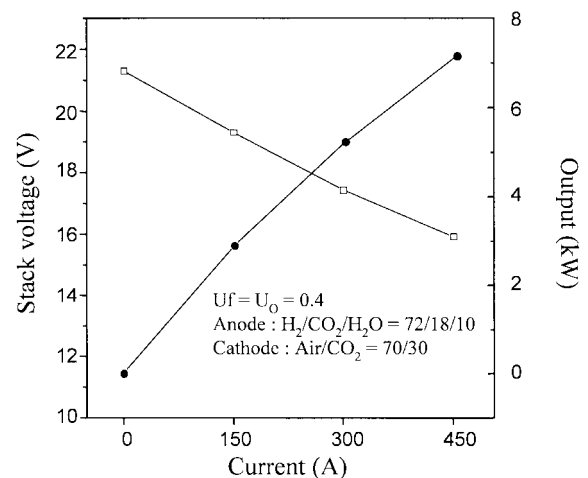


Fig. 3. Initial performance of 6 kW stack.

respectively. The calculated power at 150 mA/cm² was 7.02 kW, 1 kW higher than the designed value. The measured OCV was higher by 20 mV than the theoretical one. The reason was thought to be the lower temperature of the cells located in the middle. The performance of the stack continuously increased until 1,000 hours showing maximum power of 7.6 kW. The same behavior was also found in single cell operation, but the time to reach maximum performance was usually less than 500 hours. The size difference might be a main reason for the delayed time. As shown in Fig. 2, it takes time for the cathode to be adequately oxidized and lithiated. Polarization comparison by each source with single cell showed interesting results as summarized in Table 4. Despite that the total polarization was almost identical with each other, NL of the stack was larger by 20 mV, but vice versa for the electrode polarization. As a matter of course, the larger the area becomes,

Table 4. Polarization analysis: stack vs. single cell

| Polarization | 6 kW stack | Single cell |
|--------------|------------|-------------|
| Total | 247 mV | 240 mV |
| IR | 52 mV | 42 mV |
| Electrode | 97 mV | 118 mV |
| NL | 98 mV | 80 mV |

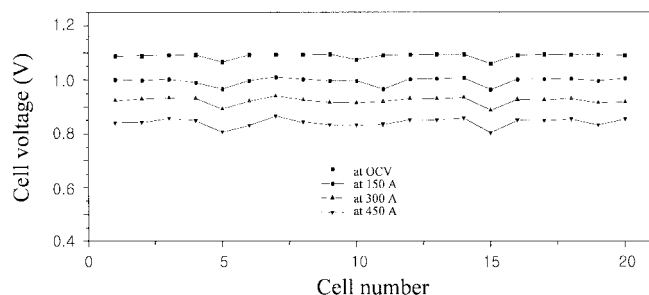


Fig. 4. Voltage distribution of 6 kW stack.

the higher the NL that is anticipated. But the reason for the smaller electrode polarization of the stack still requires more investigation.

2-2. Voltage Distribution

Voltage distribution of a stack totally depends on the degree of uniformity of components and on the level of separator design and fabrication. Fig. 4 shows the excellent voltage distribution of the 6 kW stack. The standard deviation was a mere 3 mV, far better than our expectation. The biggest deviations were found in the No. 5 and No. 15 cells without Al coating. The other cells except No. 10 were protected from corrosion attack with Al coating. It was very difficult to apply Al coating to such a thick temperature plate without having distortion during the diffusion process after coating. Wet seal areas of those plates were much more susceptible to corrosion, which led to a voltage drop due to gas leakage.

2-3. Effect of Fuel Utilization

When fuel utilization goes up, in other words, the flow rate of fuel decreases at the same electrical load condition, the voltage of a stack usually decreases in response to the polarization increase (activation & concentration) and to the changing gas composition. The magnitude of the voltage drop with fuel utilization variation was reported as about -1.5 mV for 1% increase in fuel utilization at the current density of 150 mA/cm² [Tanaka, 1989]. When fuel utilization increased from 40% to 80%, the 6 kW stack voltage decreased from 17.05 V to 15.94 V indicating -1.38 mV/% fuel utilization/unit cell at a current density of 150 mA/cm². As shown in Fig. 5 that depicts the voltage variation of each unit cell in the 6 kW stack with increase of fuel utilization, the stack showed uniform voltage distribution regardless of fuel utilization level. This could be regarded as another evidence for the excellent separator design in terms of fluid dynamics.

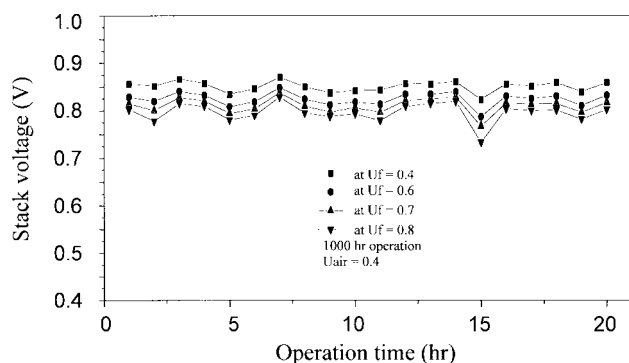
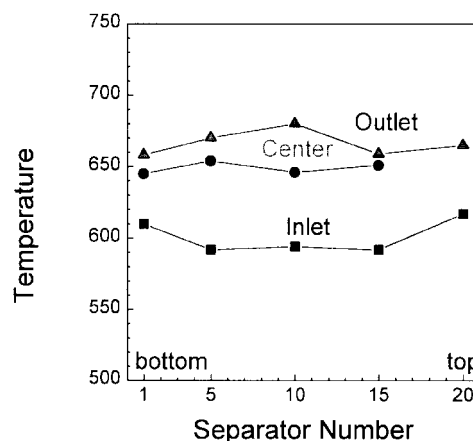
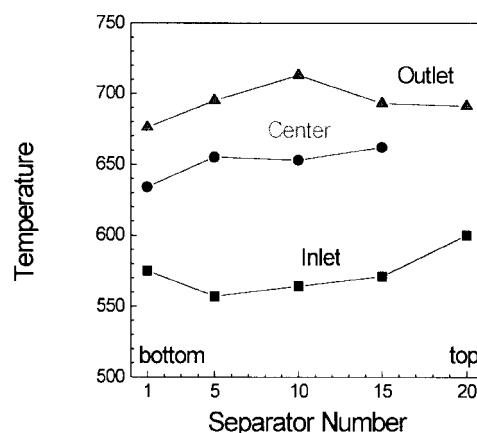


Fig. 5. Effect of fuel utilization.



(a) Temperature distribution at 100 mA/cm²



(b) Temperature distribution at 150 mA/cm²

Fig. 6. Temperature distributions of 6 kW stack.

2-4. Temperature Distribution

The importance of temperature distribution in a stack, particularly under load, cannot be overestimated because it affects the lifetime of a stack to a significant extent. At a temperature above 680 °C, stack components deteriorate too fast to maintain their expected lifetime. On the contrary, at a temperature below 580 °C, a stack usually performs poorly due to high ohmic polarization and electrode polarization. Therefore, it is a rule of thumb in designing a stack to operate in the temperature range of 580 – 680 °C. The 6 kW stack was also designed to behave in the same manner. Fig. 6 describes the temperature distributions in the 6 kW stack under load. Since fuel and oxidant gases flow in a co-flow direction, the temperature of a given separator tends to increase with gas flow direction due to the exothermic electrochemical reaction. As a result, the outlet side has the highest temperature in a particular separator. When operated at a current density of 100 mA/cm² and 60% and 40% for fuel and oxidant utilization, respectively, the highest temperature of 680 °C occurred at the outlet side of the No. 10 separator that is located at the center of the stack. The lowest temperature of the stack, meanwhile, was measured as 592 °C at the inlet side of the No. 5 separator. This satisfied the design criterion very well. When the current density increased to 150 mA/cm², however, the measured temperature range strayed from the design criterion by 33 °C for the maximum limit

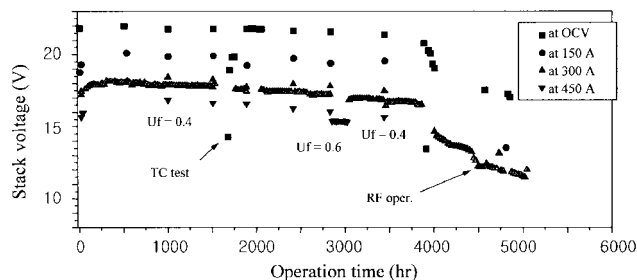


Fig. 7. Long-term performance of 6 kW stack.

as well as by -23°C for the minimum limit. To solve this temperature control problem, cathode gas recycle should be adopted for cooling at the expense of stack performance. However, cathode gas recycle with an enormous quantity of oxidant gas brings another problem of intolerable pressure drop at the cathode manifold, which may result in breakage of matrix. Therefore, stack operation at elevated pressure is required to reduce the pressure drop. Based on this result, the 25 kW stack scheduled at the end of 1999 will be operated at 3 atm with cathode recycle ratio of 4.2-5. Endurance

As operating time elapses, the cell voltage will decrease due to the increase of polarization by micro-structure changes of porous components, loss and redistribution of electrolyte, etc. The target of the 6 kW stack was to maintain its decay rate under $1\%/1,000$ h for at least 2,000 hours. The long-term performance of the stack is depicted in Fig. 7. Up to 3,000 hours, the decay rate was measured as only $0.15\%/1,000$ h, although there had been an unexpected thermal cycle due to the failure of fuel pre-heater around 1,800 hours. However, the effect of the thermal cycle came into play later on. After 2,000 hours OCV drop along with stack voltage became apparent, very slow in the beginning though, then the decay rate accelerated with operating time regardless of the application of load. At the same time the temperatures of upper unit cells increased abnormally, indicating hot spot formation due

to gas crossover. It was believed that the thermal cycle without proper control caused cracks of matrix. And this unusually high temperature delivered bad effects throughout the whole unit cells.

Even though the 6 kW stack experienced the difficulty in temperature control under full load, it went through 4,860 hours of load operation out of 5,760 hours of its total operation time, while accumulating electricity of 23,202 kWh.

CONCLUSIONS

The 6 kW MCFC stack operation made by in-house technology alone performed very well over its design target in every respect: initial performance, lifetime, decay rate and voltage distribution. During 5,600-hour operation it succeeded in generating total electricity of 23,202 kWh. It was also confirmed that cathode gas recycle at elevated pressure must be introduced to control the stack temperature properly, particularly for a stack over 5 kW in capacity.

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