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Effect of operating temperature on the performance of molten-carbonate fuel cells

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Abstract

The influence of operating temperature on the performance of molten-carbonate fuel cells performance is investigated by using experimental cells and other investigative analysis. The results indicate that the operating temperature should be kept within the range of 650 to 700 °C from the viewpoint of the cell voltage. A temperature of 675 °C is found to yield optimum cell life. Loss of electrolyte severely accelerated degradation of the cells.

Introduction

Fuel cells, especially molten-carbonate fuel cells (MCFCs), are promising alternatives to conventional power-generation systems because of their high efficiency, excellent environmental features, and the possibility of cogeneration. Usually, MCFCs are operated and around 650 °C, at which temperature the electrolyte is molten and serves as a good ionic conductor. The latter property cannot be achieved at lower temperatures. On the other hand, corrosion of cell components is accelerated in the presence of molten carbonate at higher temperatures. In addition to this disadvantage, a loss of molten carbonate can easily occur because of its increased vapour pressure at higher temperatures [1]. Therefore, it is important for MCFC systems to overcome the effect of operating temperature on cell performance.

Practical MCFCs take the form of a stack composed of several cells. Such stacks may exhibit a certain degree of temperature variation [2]. It is important to achieve a uniform temperature distribution in both the vertical and the horizontal directions. As a result of resistance (IR) effects, a temperature distribution of over 100 °C can be experienced in cells [2, 3]. In order to achieve uniformity in temperature, the flow of oxidant gas is controlled during stack operation. For example, heat (which is generated by fuel cell reaction) is usually removed by oxidant gas cooling. The optimum operating temperature should be determined in order to obtain maximum cell performance.

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In this paper, an investigation is made on the effects of operating temperature on both the initial performance and the long-term operating characteristics of a MCFC system.

Experimental

Test cells (surface area of 25 cm^2) were assembled as follows. The cathode consisted of a sintered nickel plate with a thickness of 0.76 mm. Using a model 9310 porosimeter (Shimadzu Seisakusho Co. Ltd.), the porosity was found to be 70 to 75%. The anode was made from nickel–aluminum alloy powder (Mitubishi Materials Co. Ltd.). This electrode had a thickness of 0.76 mm and a porosity of 50 to 55%.

The Li_2CO_3 and K_2CO_3 powder comprising the electrolyte were guaranteed chemicals (Foote Minerals Co. Ltd). The eutectic proportions of Li:K were 62:38 by atomic ratio. The electrolyte supporting plate consisted of $LiAlO_2$ powder (H-14, Foote Minerals Co. Ltd.) and was fabricated by the tape-casting method. The thickness was 0.5 mm and the porosity was 50%. The eutectic electrolyte was maintained at the required atomic ratio and was soaked into both electrodes when the cell temperature reached 650 °C.

The cell construction is shown in Fig. 1. The cell frame and gas pipes were made with 316L stainless steel. Perforated nickel served as the current collector for the anode and 316L stainless steel was used for the cathode.

Cells were operated between 550 and 750 °C by controlling the output of heaters that were located at the side of the cell frames. The composition of the fuel and oxidant gases was 56% H_2/14% CO_2/30% H_2O and 70% air/30% CO_2, respectively. The gases were preheated to around 650 °C before entering the cells. The gas utilization, U_f/U_{ox}, was 40%/40% at 150 mA cm^{-2} in the initial cell performance measurement, and 14%/13% during the endurance test. The N_2 cross-over was measured every 500 h under the condition of $U_f/U_{ox} = 40\%/40\%$ by gas chromatography (GP-3, Shimazu Seisakusho Co. Ltd.).

Cell resistance was checked with four-probe a.c. impedance meters (4328 A, Yokogawa Ltd.). The cells were disassembled after testing. Each cell component was analyzed using the techniques of X-ray diffractometry

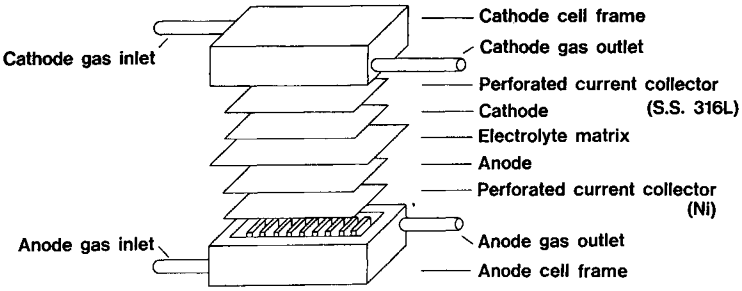


Fig. 1. Cell construction.

(RAD-C, Rigaku Denki Co. Ltd.) and scanning electron microscopy (DS-130, AGT Co. Ltd.). The molten carbonate contents in each component were calculated as the weight loss by extracting carbonate with a mixture of 70% acetic acid and 30% anhydrous acetic acid.

Results and discussion

Both the open-circuit (*OCV*) and closed-circuit (*CCV*) voltages were compared at 150 mA cm^{-2} for various operating temperatures between 550 and 750 °C. The results are shown in Fig. 2. The observed *OCV*s were almost the same as those calculated from the Nernst equation. As shown in Table 1, there is a significant dependence of the *CCV* on the operating temperature in the lower temperature range [4]. By contrast, the influence on the *CCV* in the high temperature range between 700 and 750 °C was very small so

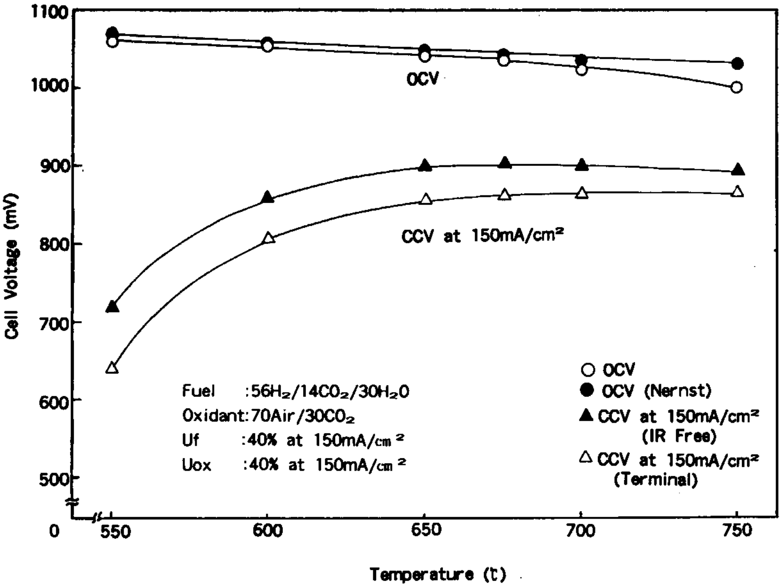


Fig. 2. Relationship between cell voltage and operating temperature.

TABLE 1

Dependence of cell voltage on operating temperature

Temperature (°C)	Terminal voltage (mV/°C)	IR-free voltage (mV/°C)
550~600	3.5	3.0
600~650	1.0	0.8
650~700	0.2	0
700~750	0	−0.2

that cells exhibited almost the same performance. Voltage improvement is not expected above 700 °C. The $V_{\text{IR-free}}$ between 650 and 700 °C was 0 mV/deg., i.e., the electrode activity was constant above 650 °C. These findings suggest that a temperature range between 650 and 700 °C, provides optimum cell performance.

The endurance test was carried out for 1000 h; the results are given in Fig. 3. The cell operated at 550 °C was discharged at 100 mA cm^{-2} from the start of testing. The cell operated at 750 °C was discharged at 150 mA cm^{-2} for 300 h and was then discharged at 100 mA cm^{-2} because its polarization was high. The remaining cells were discharged at 150 mA cm^{-2}. The degradation rates of the cells are summarized in Table 2. It can be seen

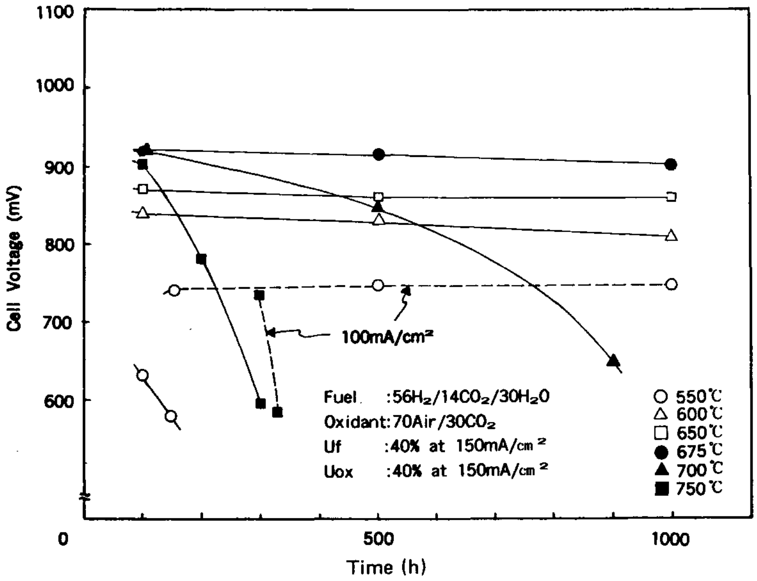


Fig. 3. Dependence of cell voltage on operating temperature.

TABLE 2

Degradation rates of cells[a]

Temperature (°C)	Degradation rate (mV/1000 h)	Remarks
550	1	$CD = 100$ mA cm^{-2}
600	30	
650	20	
675	30	
700	270 (60 mV/500 h)	
750	330 mV/300 h	stopped the discharging at 500 h

[a] Fuel: 56% H_2/14% CO_2/30% H_2O; oxidant: 70% air/30% CO_2; U_f/U_{ox}: 14%/13% at 150 mA cm^{-2}.

that operating temperatures below 675 °C did not exert any significant effect on the cell degradation rate [5]; the value was about 30 mV/1000 h. Above 700 °C, however, a marked acceleration in cell degradation was observed.

Changes in cell resistance and N_2 cross-over in the anode exhaust gas were measured in order to verify the above phenomena. Figure 4 shows the dependence of the cell resistance upon the operating temperature; the resistance was measured at the *OCV*. The data show that the resistance at 700 and 750 °C gradually increased during cell operation. By contrast, the other cells exhibited stable performance. This behaviour is similar to that shown previously in Fig. 3. The variation in N_2 cross-over, given in Fig. 5, is in accordance with the cell-resistance characteristics (Fig. 4). The results of Figs. 4 and 5 support the fact that loss of electrolyte was responsible for cell degradation when the operational temperature was above 700 °C. Overall, it is concluded that the cell temperature should be kept below 675 °C in order to maximize cell life.

After discharge testing, each cell was disassembled and subjected to a post mortem. It was found that the cathode of the cell operated at 750 °C was reduced to nickel metal on the opposite side of the anode inlet. This suggests that the loss of electrolyte caused the reactant gases to cross over by passage through the matrix. The same phenomenon was observed in the cell that was operated at 700 °C. Each component was subjected to X-ray diffraction phase analysis. It was found that the composition of the anode, cathode and matrix did not alter, either before or after discharge and irrespective of the operating temperature. Each component showed chemical stability up to 750 °C. As shown in Fig. 6, however, the ratio of α phase to γ phase for $LiAlO_2$ gradually increased as the operating temperature was raised. Scanning electron microscopy was carried out on the anodes, cathodes

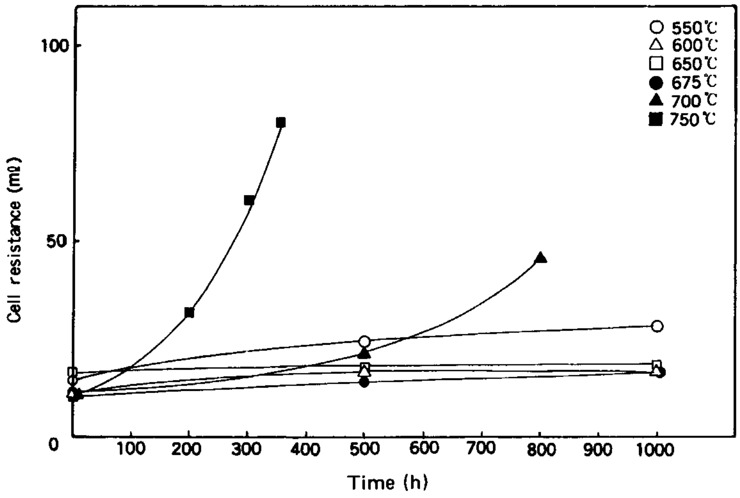


Fig. 4. Dependence of cell resistance on operating temperature.

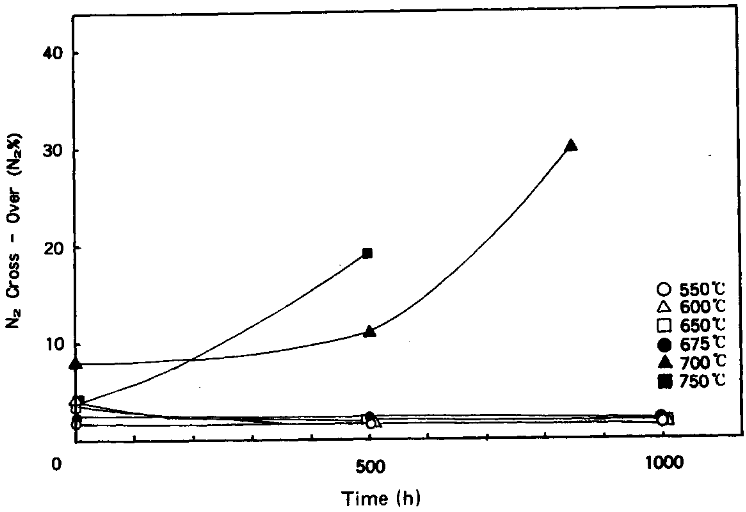


Fig. 5. Dependence of N_2 cross-over upon operating temperature.

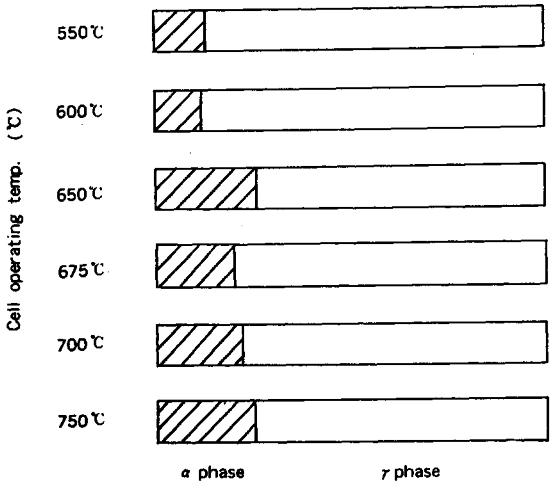
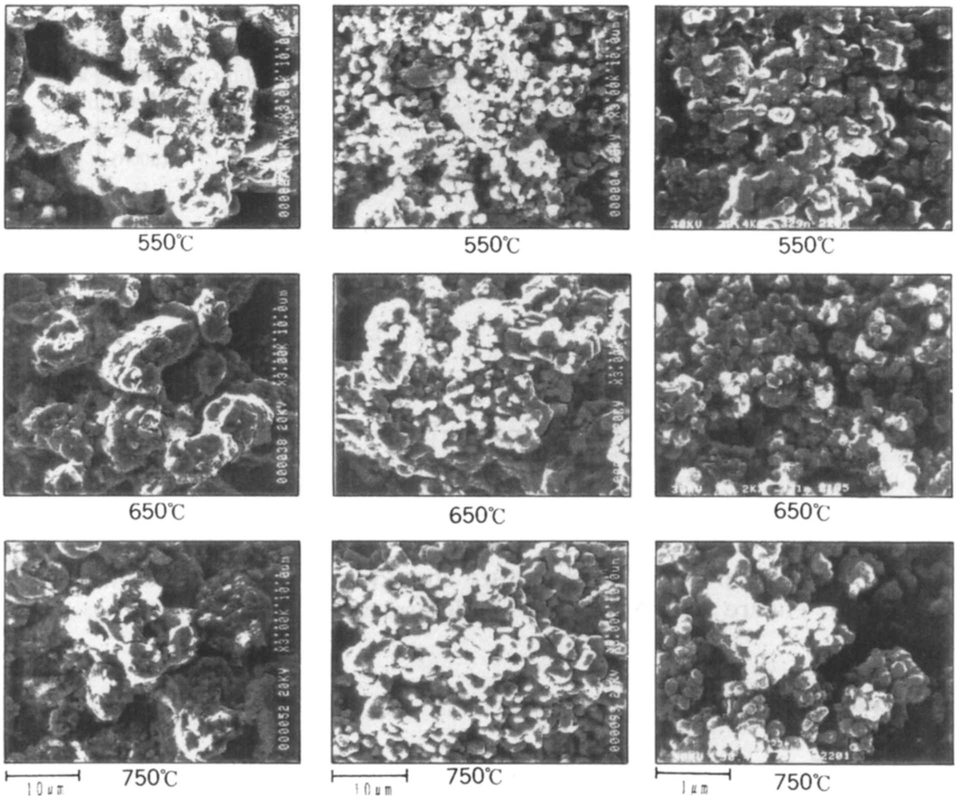


Fig. 6. Influence of cell operating temperature on $\alpha \rightarrow \gamma$ phase formation.

and matrices in order to investigate any changes in the microstructure. The electron micrographs are shown in Fig. 7. No significant differences, such as growth in particle-size, were observed. The anode displayed a tendency to creep at high temperature but this had little effect on electrode thickness, as shown in Table 3. It was confirmed that each component had sufficient mechanical strength to withstand operation between 550 and 750 °C.

Figure 8 shows the electrolyte retention in each component after the cell discharge test. The total electrolyte retention was between 70 and 80%/ 1000 h at 675 °C, but decreased to 50%/1000 h and 50%/500 h at 700 and 750 °C, respectively. In other words, the electrolyte disappeared at higher



(a) (b) (c)

Fig. 7. Electron micrographs of cell components: (a) anode, (b) cathode, (c) matrix.

TABLE 3

Change of anode thickness with cell operating temperature

Temperature (°C)	Change of anode thickness (µm)
550	−2
600	±0
650	+11
675	±0
700	+2
750	−3

cell operating temperatures, especially above 700 °C. Whereas the electrolyte retention in the anode remained almost constant, that in the cathode and the matrix decreased suddenly at 700 °C. This finding supports the conclusion that electrolyte retention in the matrix was responsible for the increase in the cell resistance, N_2 cross-over, and the degradation of cell performance.

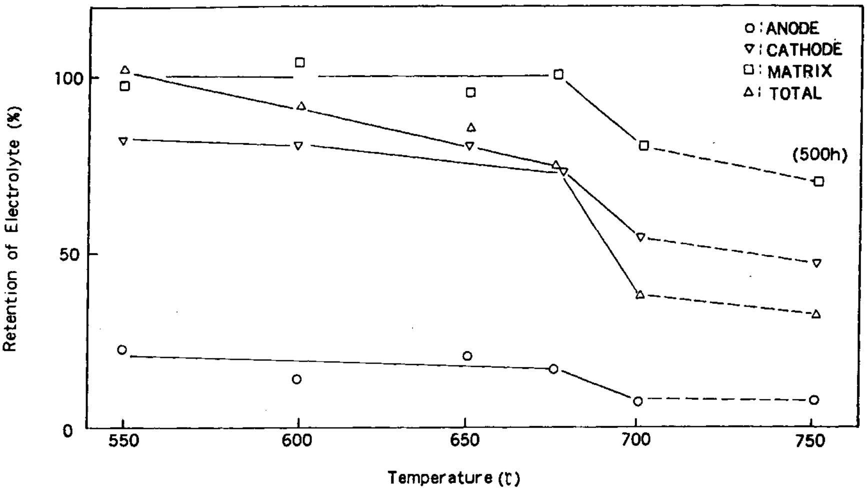


Fig. 8. Influence of cell operating temperature on electrolyte retention.

Clearly, the cell operating temperature should be maintained below 675 °C in order to ensure good retention of electrolyte.

Conclusions

The effect of operating temperature on the performance of a MCFC system has been studied in detail using experimental cells and various investigative techniques. The results are as follows:

(1) From the viewpoint of cell voltage, the optimum temperature range is 650 to 700 °C.

(2) To ensure good cell life, the cell temperature should be kept below 675 °C.

(3) Cell degradation occurs above 700 °C and is caused by loss of electrolyte.

Acknowledgement

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