Evaluation of Longer Life for MCFC Using Single-cells

Background
Molten carbonate fuel cell (MCFC) is expected to be used in power generation systems, having high efficiency and lower emissions of NOx and SOx. Thus MCFC is a power generation technology that can apply widely to power generating systems. MCFC, however, needs to have 40,000 hours longevity for commercial power plants, but internal nickel short-circuiting (Ni-shorting) is a barrier to achieving this longevity target. Various strategies are proposed as preventive measures of Ni-shorting, and finally, it is necessary to apply these strategies to small bench-scale single cell examination, and to confirm the availability of preventive measures under actual operating conditions. Another obstacle to long service life is performance decay with operating time. In order to clarify factors related to performance decay, it is necessary to conduct longer time operation tests and performance analysis.

Objective
The objective is to evaluate longer life for MCFC using small single cells by verifying the availability of preventive measures for Ni-shorting, and accumulating prolonged operating data.

Principal Results
1. Acceleration test of Ni shorting
(1) It was verified that the starting time of Ni-shorting became longer by applying the advanced components (1: MgFe₂O₄ (Fe/Mg) coated cathode, 2: additives (BaCO₃ and CaCO₃, Ba/Ca) into electrolyte, 3: electrolyte of 70% Li₂CO₃ and 30% Na₂CO₃ (Li/Na = 70/30%), and 4: α-type LiAlO₂ for electrolyte matrix (Table 1).
(2) Based on the assumption of independence of the above effects (1 to 3), the starting time of Ni-shorting with three advanced components simultaneously was estimated at about 36,500 hours and agreed with that time estimated by the experimental result in FY2002.
(3) It was clear that the acceptable upper Ni deposition limit in a pore of the α-LiAlO₂ matrix at the starting time of the Ni shorting increased compared with that of γ-LiAlO₂ (Fig.1).
(4) It was clarified that the effects of thickness of electrolyte matrix, cathode partial pressure, and temperature for the starting time of Ni-shorting were estimated in the cells with the α-LiAlO₂ matrix (Fig.2).

2. Long-term operation tests for life time
It was clarified that voltage decay depends almost completely on increasing internal resistance, and the resistance increase with time is mainly caused by electrolyte loss in the cell (Fig.3). And the cell voltage estimated by the cell lifetime estimation method developed by CRIEPI agreed with the measured cell voltages. It was capable of accurately predicting the long-term performance of MCFC (Fig.3).

As a result, we estimated durability for Ni-shorting over life of 40,000 hours. Consequently, we obtained data from continuous operation of over 37,000 hours, and we verified that MCFC can maintain performance and durability over the long term.

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It was verified that the starting time of Ni-shorting became longer by applying the advanced components (1: Fe/Mg coated cathode, 2: additives (Ba/CaCO3) into electrolyte, 3: electrolyte of Li/Na2CO3 = 70/30%, and 4: a-type LiAlO2 for electrolyte matrix.)

Table 1 Summary of acceleration test results

<table>
<thead>
<tr>
<th>Focus</th>
<th>Advanced Components</th>
<th>Estimated starting time of Ni-shorting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base data</td>
<td>Electrolyte Li/Na</td>
<td>14,500 hours</td>
</tr>
<tr>
<td>Advanced Cathode</td>
<td>Ba/Ca Additives (mol%)</td>
<td>Normal</td>
</tr>
<tr>
<td>Electrolyte composition</td>
<td>Mg/Fe coated</td>
<td>21,500 hours (1.5 times)</td>
</tr>
<tr>
<td>Additives into electrolyte</td>
<td>3/3</td>
<td>Normal</td>
</tr>
<tr>
<td>Matrix material</td>
<td>60/40</td>
<td>a-type LiAlO2</td>
</tr>
</tbody>
</table>

The acceptable upper Ni deposition limit in a pore of the a-LiAlO2 matrix at the starting time of Ni-shorting increased compared with that of γ-LiAlO2.

Fig.1 Acceptable upper Ni deposition limit in matrix on pore volume

(1) The voltage decay depends almost completely on increasing internal resistance caused by electrolyte loss in the cell.
(2) It was capable of accurately predicting the long-term performance of MCFC.

Fig.2 The effect of the matrix thickness, cathode CO2 partial pressure, and the temperature on Ni shorting time for a-type LiAlO2.

We estimated the effect of the matrix thickness, cathode CO2 partial pressure, and temperature on the starting time of the Ni shorting for a-type LiAlO2.

Fig.3 Longest durability test result of a bench-scale cell and predictive value