NiO Cathode Dissolution and Ni Precipitation in Li/Na Molten Carbonate Fuel Cell.

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1. INTRODUCTION

The lifetime of a molten carbonate fuel cell (MCFC) is shortened by the dissolution of the lithiated nickel oxide cathode. Application of a mixture of 52mol% Li_2CO_3 and 48mol% Na_2CO_3 (Li/Na) melt as the electrolyte of the MCFC is expected to achieve higher voltage and longer lifetime due to its higher ionic conductivity and lower solubility of the nickel oxide cathode. In this paper, a series of Li/Na cells with various matrix thickness has been tested at different cathode CO_2 partial pressure and temperature conditions systematically to develop the prediction equations for starting time of nickel short-circuiting. Moreover, the dependence of precipitated nickel distribution on temperature was measured.

2. EXPERIMENTAL

The tests have been carried out in single cells with constant fuel and oxidant gas composition. These gas conditions were set at $H_2/CO_2/H_2O$=56/14/30%, and $O_2/CO_2/N_2$=15/60/25%. Gas utilizations were set as fuel utilization=40%, O_2 utilization=40%, and CO_2 utilization =20%. High concentration of 60% CO_2 gas in the cathode were applied to the single cells to accelerate the nickel short-circuiting phenomenon in this study. The cells were continuously operated at 150 $mAcm^{-2}$. The operating temperature was varied from 873 to 973 K to evaluate the effect of temperature. The dependence of the nickel particle distribution on temperature has been evaluated using an image processing method.

3. RESULTS AND DISCUSSION

The measured starting time of nickel short-circuiting for the Li/Na cells is expressed as follows;

$$t_{sc} = 7.63\times10^{8}\times L^{2.05}\times P_{CO2}^{-0.76}\times\exp(-54.8\times10^{3}/RT)$$

The starting time of nickel short-circuiting (t_{sc}) is approximately proportional to the second power of the matrix thickness (L) and the minus 0.76ths power of the cathode CO_2 partial pressure (P_{CO2}). Moreover, the starting time of nickel short-circuiting was found to be longer with higher temperature.

The changes in the precipitated nickel particle distribution per unit of matrix cross sectional area with operating temperature are measured as shown in Fig. 1. The precipitated nickel distribution peak shifts to the anode side with higher temperature. It can be considered that precipitated nickel easily advances toward the anode in the case of 973K with convection of the molten carbonate from the cathode to the anode compared with that in operation at 873K. The peak was also found to shift toward the anode with time at same temperature by other tests.

The relationship between the conductivity and the volume ratio of the nickel in the matrix is shown in Fig. 2. It shows the volume ratio of the nickel particles is calculated to be around 4.45% of the active volume in the matrices when the nickel short-circuiting has started.

4. CONCLUSIONS

The starting time of nickel short-circuiting was found to be longer with higher temperature. In the case of operation at 973K, the peak position of Ni particles is advanced toward the anode faster than that in operation at 873K. The volume ratio of the nickel particles is calculated to be around 4.45% of the active volume of the matrices when the nickel short-circuiting has started.

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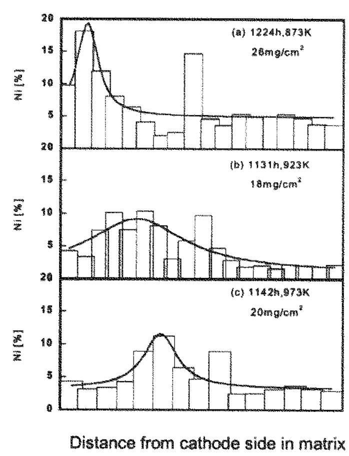

Fig. 1. Changes in precipitated nickel particle distribution per unit of cross sectional area with operating temperature(time range 1100-1200hr) after short-circuiting.

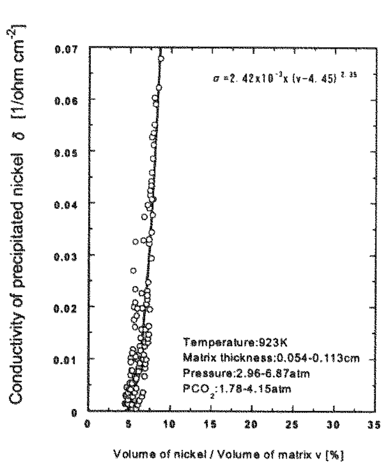

Fig. 2. The relationship between conductance of the short circuit and the volume ratio of precipitated nickel in the matrix