

## Electrode Reaction Characteristics with Inert Gas Step Addition (ISA) Method in Molten Carbonate Fuel Cell

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A fuel cell, as a prospective electric power source, is an electrochemical reaction system. Fast electrode reactions are preferable to achieve good performance in the fuel cells. The molten carbonate fuel cell (MCFC) provides a fast electrode reaction through carbonate melt as an electrolyte, working at a relatively high temperature around 923 K and using porous electrodes with sufficiently large surface areas.

The electrochemistry for the fuel cells has been focused mostly on the transport processes in the solid and liquid phases. It is available when the electrode reaction is slow enough to be confined within those phases. However, the MCFC with very fast electrode kinetics and rather thin electrolyte films on the electrode surfaces requires an extension of the investigation for the mass-transfer effect up to the gas phase.

In this work, the mass-transfer effects in the gas and liquid phases were investigated through overpotential analysis in 100 cm<sup>2</sup> class MCFCs. An inert gas step addition (ISA) method, as a novel experimental tool, was employed to measure the overpotentials.<sup>1)</sup> ISA was carried out by adding an inert gas to the reactant flow of an electrode at a certain distance from the cell. Thus it varied the flow rate and partial pressure of reactants in the cell, resulting in an overpotential shift due to the mass-transfer rate changes in the phases.

MCFCs used in this work were 100 cm<sup>2</sup> class single cells. Details of the cell components, fabrication, and operating apparatus have been described in a previous work.<sup>1)</sup> Nitrogen was used as the inert gas and addition amount was controlled with a mass flow controller in a range from 0.1 to 1.0 l/min. Four distances from the inert gas addition port to the cell, 0.8, 1.5, 4.0, 4.8 m were adapted with 4.8 mm inner diameter tube at both electrodes. The anode gas was a mixture of 80 mol% H<sub>2</sub> and 20 mol% CO<sub>2</sub>, which was fed through a humidifier at 53°C. A gas mixture of 70 mol% air and 30 mol% CO<sub>2</sub> served as the cathode gas. Utilization of the anode gas ranged from 20 to 60% and that of the cathode gas was between 40 to 60% at currents of 15 A. All experiments were carried out at 923 K under atmospheric pressure.

Figure 1 shows open circuit voltage ( $E_{OCV}$ ) and voltage shifts at various tube lengths by the addition of 0.3 l/min nitrogen to the anode.  $E_{OCV}$  and voltage curves at the tube lengths are arbitrarily arranged in the figure to compare the differences among them. Increase of  $E_{OCV}$  is observed according to the nitrogen addition. Since  $E_{OCV}$  is determined by the following relation (Eq. 1), nitrogen in the cell reduces the partial pressure of reactants and increases  $E_{OCV}$ .

$$E_{OCV} = E^{\circ} + \frac{RT}{nF} \ln \left( \frac{P(H_2)P(O_2)^{0.5} P(CO_2)_{ca}}{P(CO_2)_{an} P(H_2O)} \right) \quad (1)$$

where  $E^{\circ}$  is the standard potential, and the subscripts 'an' and 'ca' denote the anode and cathode, respectively. All other symbols have their usual meaning. It is clearly observed that the onset time of  $E_{OCV}$  depends on the tube length, because longer length requires more time for the

added nitrogen to reach the cell.

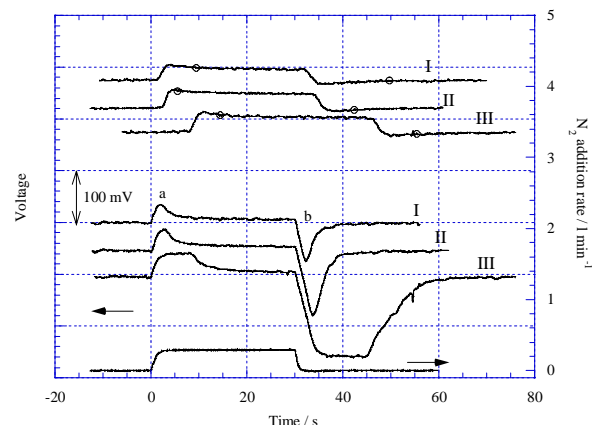


Fig. 1 Comparisons of the voltage shift patterns by the addition of 0.3 l/min N<sub>2</sub> to the anode with various tube lengths at anode inlet flow rate = 0.253 l/min ( $u_f=0.6$  at 15 A), cathode inlet flow rate = 0.883 l/min ( $u_{ox}=0.4$  at 15 A), 923 K, 1 atm. I: Tube length = 0.8 m, II: 1.5 m, III: 4.8 m. Line with circle:  $E_{OCV}$ , Bare line: Voltage at 15 A

The voltage shift at the 15 A of polarization state shows quite difference from that of OCV and a strong dependence on the tube length, as shown in Fig. 1. Two of voltage peaks are observed and they become wider with increasing tube length. Since the voltage difference between  $E_{OCV}$  and the voltage at the polarization state is a total voltage loss, the 'a' and 'b' peaks result from the change of voltage loss. It has been suggested in a previous work<sup>1)</sup> that the anode reaction is mainly a mass-transfer control process in the gas phase and overpotential relation can be expressed by gas-phase mass-transfer rate. Since the gas-phase mass-transfer rate is a function of gas flow rate,<sup>1)</sup> the peaks can be ascribed to the overpotential shift due to the mass-transfer effect in the gas phase by the flow-rate change of reactants. The 'a' peak results from the reactant flow rate increasing during the arrival of added inert gas at the cell, while the 'b' peak is due to the flow rate decreasing by the interruption of the inert gas. Thus, a longer tube shifts the reactant flow rate for longer time, resulting in a wider peak. The voltage peak's behavior confirms that the anode reaction is a gas-phase mass transfer control process.

The ISA measurement at the cathode showed much smaller 'a' peak than that of the anode, indicating that the gas-phase mass-transfer resistance is relatively small at the cathode. The ISA also revealed that the cathode reaction is mostly liquid-phase mass-transfer control process.

Quantitative analysis of the 'a' peaks at the anode and cathode gave following anodic ( $\eta_{an,G}$ ) and cathodic ( $\eta_{ca,G}$ ) overpotentials due to the gas-phase mass-transfer resistance at various anodic ( $u_f$ ) and cathodic ( $u_{ox}$ ) utilizations.

	$u_f$ or $u_{ox}=0.2$	$u_f$ or $u_{ox}=0.4$	$u_f=0.6$	$u_f=0.8$
$\eta_{an,G}/mV$	69	98	120	138
$\eta_{ca,G}/mV$	19	27		

## Reference

- C.-G. Lee et. al, *J. Electroanal. Chem.*, 540 (2003) 169-188