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Short communication

Applicability of molten carbonate fuel cells to various fuels

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Abstract

MCFCs can utilize CO rich and H_2 lean fuel, such as gasified biomass or gasified waste as a Pt catalyst is not used and Pt poisoning by CO does not occur. This feature has become very important due to the worldwide CO_2 depression requirements. CRIEPI has developed MCFC technologies in line with a governmental program, which mainly focused on natural gas fuel. However, CRIEPI has recently been focussing on technologies for various fuel applications. Single cells and stacks were tested with various gas compositions and showed stable performance even with high CO and high fuel utilization conditions. Gasified biomass or waste can contain many kinds of impurities such as H_2S, HCl, HF, NH_3, etc. The effects of these impurities were taken into account for single cells, and the permissible limits were estimated.

Keywords: MCFC; Gasified fuels; Biomass; Waste; Impurities

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1. Introduction

Molten carbonate fuel cells were originally developed as coal gasified combined cycles both in the U.S. and Japan because of their capability to use CO, which is the main component of gasified coal gas. However, the development of the stack and the system required a lot of time, and developments up until now have mainly been focussed on natural gas fueled stacks and systems to establish the basic technologies. Meanwhile, the Kyoto Protocol has been ratified and become effective as of February 2005. MCFCs have become much more important due to the worldwide situation of CO_2 repression. Many countries have established the renewable portfolio standards (RPS) laws in order to accelerate the introduction of renewable energies. Biomass is one of the key renewable energies, and MCFCs can utilize gasified or fermented biomass as fuel. The waste disposal problem is a big issue in many cities these days; MCFCs are able to utilize gasified waste fuel. Coal gasified gas is still expected to be a fuel for future large MCFC power stations with the aim of creating an efficient and low cost power plant independent of oil and natural gas.

However, at the moment we should focus on the original target and take advantage of MCFCs' flexibility regarding fuel. CRIEPI has recently been concentrating on technologies for various fuel applications. This paper describes the evaluation and the operation technologies developed at an earlier date for natural gas utilization, followed by the test results of single cells and stacks with various kinds of fuel compositions and added impurities. The capability of applying various fuels to MCFCs is also discussed.

2. Basic technologies for natural gas fueled MCFC power plants

As many several hundred-class MCFC power plants are under operation throughout the world now, it can be said that the basic technologies of MCFCs have almost been established. In line with a Japanese governmental program, CRIEPI has been developing many kinds of MCFC-related technologies such as cell and stack operation, electrode performance evaluation, carbon formation under high pressure operation, long term performance prediction, nickel short-circuiting prevention, stack diagnosis, system performance simulation, etc.

The performance correlation equation is one of CRIEPI's major accomplishments. It has been applied to many cells and stacks to analyze their performance. It enables the evaluation of key factors affecting the cell performance, and advises us on the most effective ways to improve the performance.

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Table 1
Composition examples of various fuels

Gas composition (dry base)	Reformed natural gas	Gasified biomass gas (wood chip)	Gasified waste gas	Gasified coal gas
H_2 (vol%)	74.5	17.5	29	27
CO (vol%)	11.2	11.5	49	64
CO_2 (vol%)	11.4	16.3	16	3
CH_4 (vol%)	2.3	0	0.1	0.1
N_2 (vol%)	0.6	54.7	5.6	5.5
H_2S (vol%)	1–9 ppb		0.36	0.46
COS (vol%)	0		0.02	0.04
HCN (mg/N m^3)	0		0.01	1
NH_3 (mg/N m^3)	0		0.25	0.4

The replacement of the Li/K electrolyte by a Li/Na electrolyte is the most representative example of its application. Cells applying each electrolyte individually were evaluated under the same conditions. The Li/Na cell showed a higher performance with a higher ionic conductivity and a lower internal resistance, which was evaluated by using the correlation equation.

The eligibility of the equation was also examined for high-pressure ranges. The measured voltages under high-pressure conditions agree with the calculated results of the equation, therefore, its applicability has been proved. The equation has been improved to evaluate long-term performance and to estimate the voltage decay. It is also applied for stack internal condition simulations and system simulations obtaining many correct, realistic and reliable results.

The pressurized operation was developed by CRIEPI a long time ago, and nickel short-circuiting was first observed in Japan. CRIEPI installed many pressure test facilities including a high-pressure test facility with a pressure range of up to 5 MPa for single cells and checked the performance. The performance saturation was observed in relation to the methanation reaction in the 3 MPa pressure range. However, MCFCs can also be operated below a 2 or 3 MPa pressure range without performance saturation. Based on many single cell test results, CRIEPI has developed an equation to estimate the nickel short-circuiting time. An accelerating test method for nickel short-circuiting has also been developed, and recent single cells have applied many countermeasures, one of which is the Li/Na electrolyte; these cells were estimated to have a life expectancy of about 40,000 h even under a high pressure (1.2 MPa) operating conditions. Furthermore, CRIEPI also clarified the method to avoid carbon deposition under high-pressure operation.

Using these evaluation methods, CRIEPI has evaluated large 100 kW-class stacks for 1 MW plants and has also demonstrated a long-term operation of a 10 kW short stack over 10,000 h in the context of the governmental program. The average voltage decay rate was determined at about 0.3%/1000 h, which is very close to the general target value of 10%/40,000 h. In the meantime, the long-term cell performance, which depends on the electrolyte corrosion, and the nickel short-circuiting have also been evaluated. The longest cell operation time at CRIEPI is more than 48,000 h and the cell is still under operation as of June 30, 2006.

Most of the tests and evaluations mentioned above were carried out with simulated reformed natural gas.

3. Advanced technologies for various fuel applications

3.1. Fuel compositions

Table 1 shows various kinds of fuel compositions. Compared to natural gas, the other fuels have high CO and low H_2 compositions and also contain many impurities. We would like to clarify whether MCFCs can be operated with such fuels.

3.2. Single cell performance

The single cell performance was first of all verified with CO rich fuel. It is necessary that the shift reaction is fast compared to the anode reaction to replenish the H_2 consumed at the anode. The shift equilibrium compositions were compared with the measured compositions of the fuel exhaust gases from the single cell by changing the simulated fuel compositions. There was a slight difference between the equilibrium compositions and the measured compositions under atmospheric conditions, however, they were almost equal under a 0.3 MPa pressure condition. The result is that the shift reaction is fast enough under pressurized operation.

The cell voltage shifts according to fuel gas composition. However, a similar pressure dependency was observed in every fuel composition.

There were some cases in which the long-term performance of the single cell decreased very slowly with high CO fuel. It was observed that the performance sometimes improved by adding steam to the fuel. We came to the conclusion that the wet ability within the electrodes is affected by the fuel composition and that the electrolyte maldistribution might be responsible for causing such unstable performance. CRIEPI developed a model of the electrolyte distribution and found that electrolyte stays/remains more within cathode in case of high CO fuel. To improve this situation, a new anode with a modified porosity for preventing cathode flooding was tested. Using the improved anode, the single cell showed stable performance.

3.3. Stack performance

The stack performance using various simulated fuels has been verified [1]. It is necessary to supply a large amount of CO to simulate high CO-content fuels. A CO gas producer was installed for the first time, which has an inverse-shift reactor. H_2 and CO_2

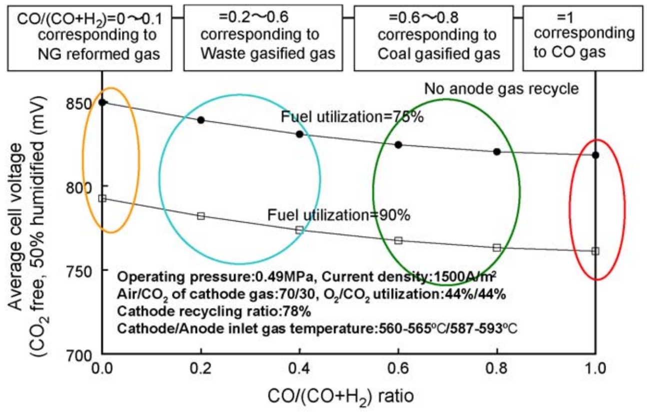


Fig. 1. 10 kW stack performance with various CO ratios.

are supplied to the reactor and CO and H_2O are produced. Some produced gas is recycled to the reactor and it can finally supply over 90% CO composition, which is balanced with CO_2. The gas producer was connected to the existing 10 kW-class MCFC test facility, which could then supply H_2, CO_2, N_2 and H_2O as fuel compositions.

The tested stack has 10 cells with a 1 m^2 commercial size reactive area. The fuel composition was set from H_2 rich gas to CO rich gas by changing the ratio of $CO/(CO + H_2)$. Fig. 1 shows the average cell voltage with a $CO/(CO + H_2)$ ratio. Even under high fuel utilization conditions, the stack shows a stable performance over a wide range of fuel compositions. The voltage at 90% fuel utilization was uniformly shifted from that at 75% utilization. It has also been verified that even if only CO (with humidification) is supplied, the single cell could generate efficient power in the MCFC.

Fig. 2 compares the H_2 concentration at the anode exhaust with the calculated H_2 value under the assumption of a shift equilibrium. Similar to single cells under pressurized operation conditions, the shift reaction was kept in equilibrium within the stack. Since the shift reaction is exothermic when H_2 is produced, supplying a high CO-content fuel generates a large amount of heat within the stack and the temperature distribution is affected. The temperature in the stack's center was observed when changing the fuel composition ratio. The measured temperature increases as the CO composition increases under fixed cathode gas recycling conditions. This agrees with the calculated value based on the exhaust fuel composition under the assumption of a shift equilibrium. It has also been proven that the shift equilibrium is fully attained in all fuel compositions.

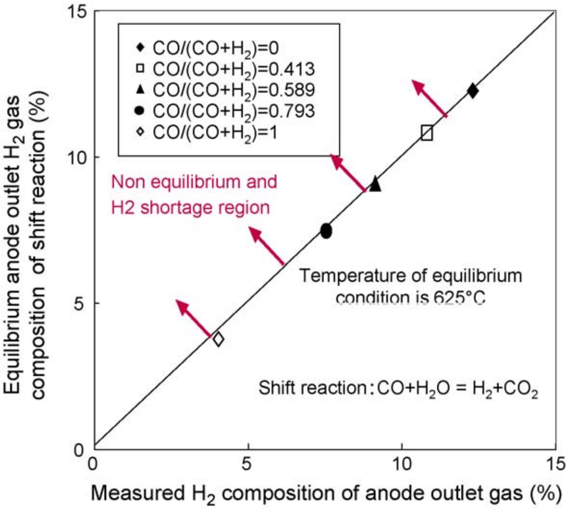


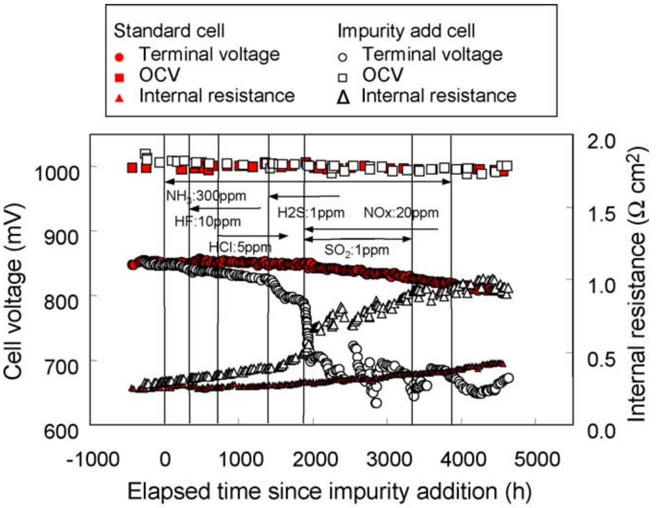
Fig. 2. Water–gas shift reaction of the stack anode outlet gas.

3.4. *Effect of impurities within various fuels*

Gasified biomass or waste contains many impurities such as sulfur, halogen, nitrogen, etc. CRIEPI has tested many single cells and evaluated the effect of such impurities by applying a simulated fuel gas containing ppm order impurities.

The test results indicate that the sulfur compound, which appears as H_2S in the fuel gas, influences the performance immensely [2]. The acceptable H_2S level is approximately 5 ppm in the case of a fuel simulating reformed natural gas with a high amount of H_2. However, a much lower level, below 1 ppm, is required in the case of a higher amount of CO-containing fuel. The decrease in performance could be caused by the delay of the shift reaction from CO to H_2 at the anode. SO_2 can be fed to the cathode through the CO_2 recycling system in MCFC plants. SO_2 in the oxidant showed similar effects to H_2S, however, it corrodes the metal hardware used as the oxidant inlet. Corrosion resistive metals such as Incoloy should be used.

Regarding halogen compounds, the cell tests were carried out for HCl and HF, which are contained in fuel gas. The addition of 10 ppm HCl has no effect on the cell voltage over several thousand hours. In the case of HF, there is also little influence on the performance over a short period of time. However, the reaction with the electrolyte leads to the accumulation of such



Temp.:650°C, Pressure:0.49MPa,
Current density:150mAcm^{-2}
Fuel: $H_2/CO/N_2/CO_2/H_2O$=10/26/13/21/30,Uf=60%
Oxidant: Air/CO_2=70/30, Uox=40%

Fig. 3. Multi impurity test.

halogens inside the MCFC and eventually large performance reduction is predicted.

NH_3 in the fuel and NO_x in the oxidant were introduced into the MCFC as a nitrogen compound without any significant reaction [3]. Furthermore, NO_x is discharged as N_2 through the electrolyte in the fuel exhaust. Therefore, the MCFC could have a kind of NO_x reducing function.

Further research on conjugated effects of such impurities has been carried out. Fig. 3 shows the multiple impurity test results. The cell performance was only affected when sulfur compounds were added. This indicates that the effects can be separated into the individual effects each impurity has.

4. Conclusions

Various fuel applications to MCFCs have been proven by the experiments of cells and a stack. The time has come to move to the next step, which includes the demonstration of these various fuel power generation systems. Some MCFC plants have started operation fueled by digester gas or gasified gas. Such gasified gases are produced by sewage water or wastewater from brewery processes. Woodchips or plastics have been gasified for some MCFC plants. Further applications using various fuels could be expected in future based on the basic test results acquired in this paper.

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