

Effect of Cyclohexene on the Performance of PEFC

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1. Abstract

Effects of cyclohexene as a candidate for odorant added to hydrogen on fuel cell performance were investigated.

When hydrogen containing cyclohexene was introduced into the cell, the cell voltage was decreased. The cell voltage drop was increased with the increase in concentration of cyclohexene.

Complete recovery in the cell voltage was observed, when addition of cyclohexene to hydrogen was terminated.

This result is applicable to system design of pure hydrogen fuel cell.

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2. Body of Paper

2.1 Introduction

Hydrogen is expected to become one of the important energy carriers in the near future for achieving a low carbon society. It is because hydrogen does not contain carbon components and no carbon dioxide (CO₂) is exhausted after using hydrogen as energy. As appliances that utilize hydrogen, fuel cells that have high energy efficiency and do not discharge pollutants are promising. Studies of fuel cell vehicles, residential fuel cell co-generation systems, etc. that use pure hydrogen as a fuel are investigated widely.

Since hydrogen is odorless, an odorant must be added just like natural gas for safety reasons. For natural gas, an odorant containing sulfur-based compounds is used, whereas in the case of hydrogen, a non-sulfur odorants are selected and studied^[1]. The most promising candidate is cyclohexene which is a hydrocarbon-based compound. Since recognition threshold value for human nose of cyclohexene is relatively high, the concentration of cyclohexene that needs to be added is several hundred times higher than the odorants that contain sulfur-based compounds using natural gas^[1].

A process flow diagram of a pure hydrogen PEFC system is shown in Fig. 1. Hydrogen is deodorized before being introduced into the cell stack, so hydrogen that does not contain cyclohexene is introduced. Since the concentration of cyclohexene is high, a large amount of deodorant is required. Due to this reason, the size of the deodorizer and the whole system becomes large. This has been one of our subjects that diminish the attractiveness of the residential pure hydrogen PEFC systems.

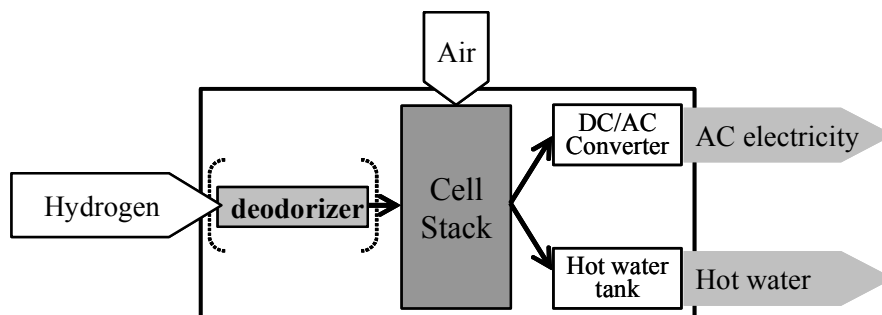


Fig. 1 Process flow diagram of a pure hydrogen PEFC system

The reason that cyclohexene needs to be removed completely by using a deodorizer is that the performance of the cell stack could severely degraded by a small amount of impurity in the fuel or air^{[2]-[6]}. However, an influence of cyclohexene on PEFC stack under the operating conditions of residential pure hydrogen PEFC systems is not clarified.

In this research, the effect of cyclohexene as a candidate for odorant added to hydrogen on cell voltage is investigated.

2.2 Experimental setup

An influence exerted on cell voltage by impurities was evaluated through a single cell testing with the standard JARI (Japan Automobile Research Institute) cell using an MEA (Membrane Electrode Assembly) of 25 cm² (5 cm square) in electrode area. The amount of platinum loading in the electrode catalysts, both the anode and the cathode, were 0.5 mgPt/cm². The current density was kept at a constant value of 0.25 A/cm² and the same current density was kept during the addition test. The utilization of fuel (U_f) was set to 90%, and the utilization of oxidant (U_o) was to 55%. The cell temperature was kept at between 65°C and 80°C, and the humidifying temperature for both the anode and cathode was set to 65°C.

The concentration of impurity was adjusted to a specified value by mixing the standard gas having a concentration higher than that of the impurity to be added, into hydrogen or air that had been already humidified. Fig. 2 shows an outline of the test equipment.

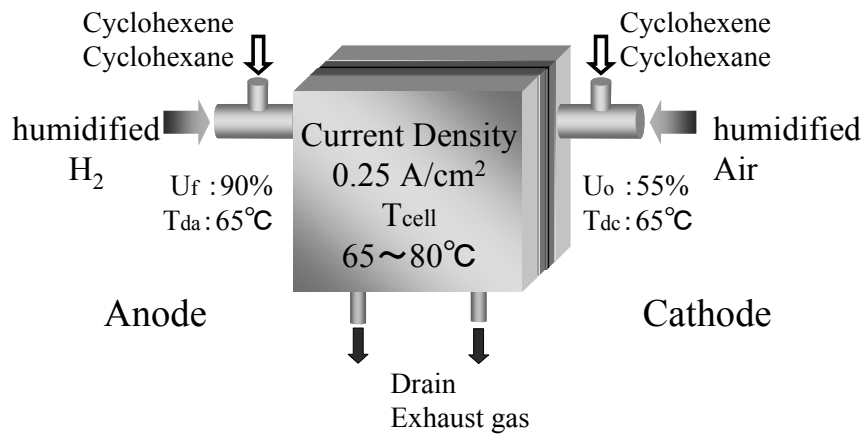


Fig. 2 Outline of test equipment

Tests for evaluating the characteristics of the cells were carried out by using the fuel cell test systems (Auto PEM, Toyo Corporation), and evaluation of cyclic voltammetry (CV), current-voltage characteristics (IV) was measured by an electrochemical measurement system (HZ5000, Hokuto Denko).

2.3 Results and discussions

2.3.1 Influence exerted on cell voltage by cyclohexene in hydrogen

At first, the concentration of cyclohexene to be added to hydrogen was increased at fixed intervals of time, and a change in cell voltage in relation to change of cyclohexene concentration was observed. Since the rate of decrease in cell voltage is high at an initial stage, the cell voltage was stabilized by performing for 200 hours without impurities. Then, cyclohexene was added by changing its concentration of 10, 100, and 500 ppm at intervals of about 100 hours. While keeping current, recovery in the cell voltage was observed by terminating addition of cyclohexene. A change in cell voltage over time is shown in Fig. 3. The dotted line in the graph shows the extrapolation of the cell voltage in the initial stage without addition of cyclohexene.

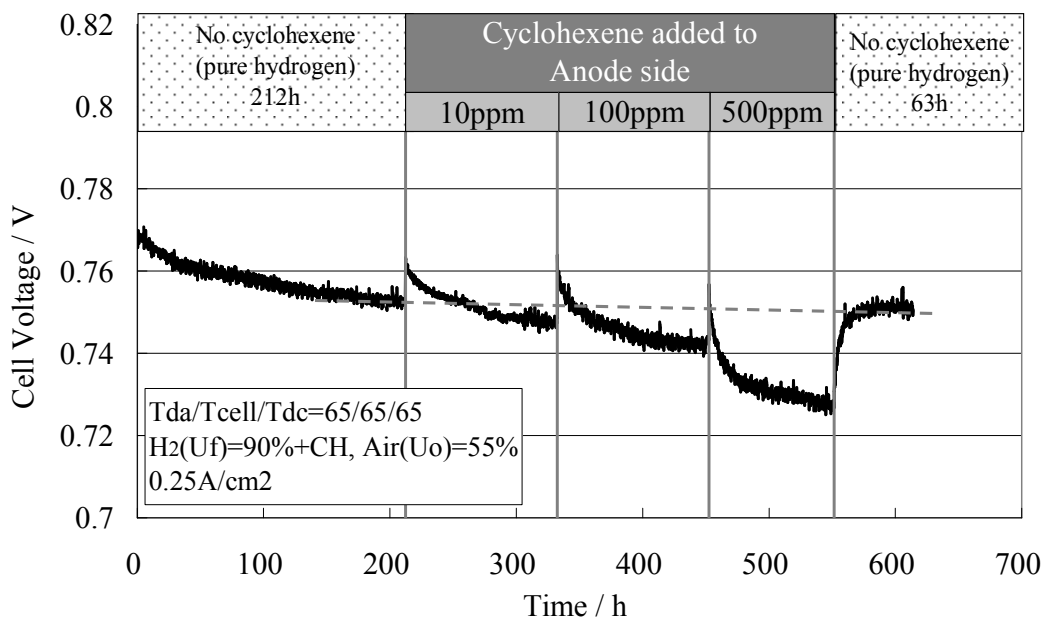


Fig. 3 The influence exerted on cell voltage by a change in cyclohexene concentration

When cyclohexene was added, the cell voltage started to decrease, but after around 50 hours, the rate of decrease gradually slowed down. The cell voltages directly before increasing the concentration of cyclohexene were compared with the extrapolated value. The cell voltage drop was increased as the concentration of cyclohexene rose, with the cell voltage being around 4, 10, 15 mV corresponding to the cyclohexene concentration of 10, 100, 500 ppm, respectively. When addition of cyclohexene was terminated, the cell voltage was increased in several hours, and recovered completely.

Next, after fixing the concentration to 100 ppm, an influence was evaluated by changing the time for addition. In order to carry out long-term evaluation, operation with pure hydrogen was carried out for about 500 hours. The evaluation was made by addition for about 400 hours first, and then the cell

voltage was sufficiently recovered by suspending the addition for about two hours, followed by addition once again for about 800 hours. The result is shown in Fig. 4.

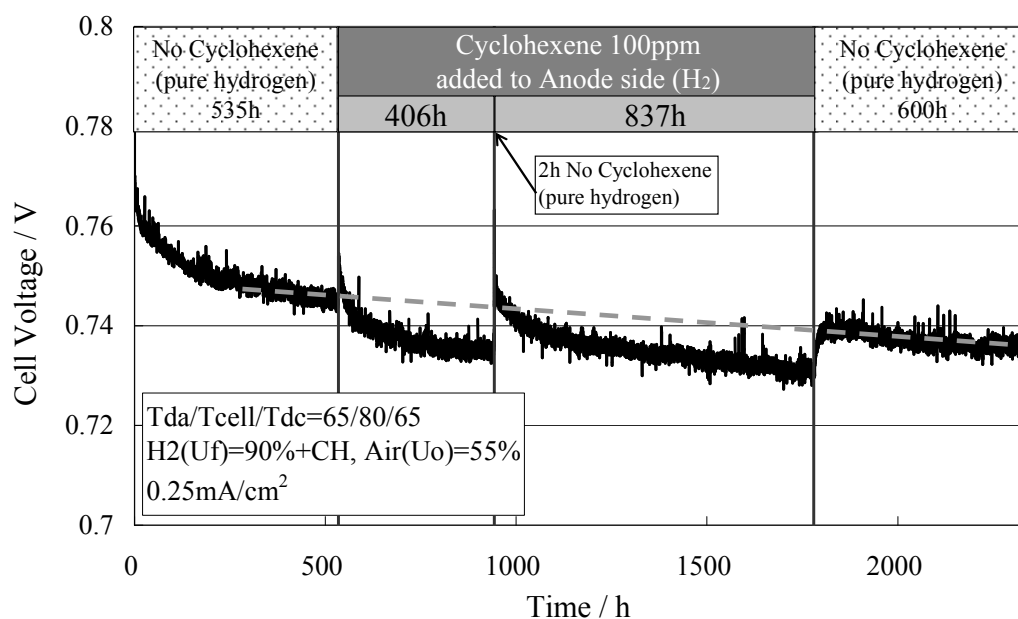


Fig. 4 The influence of time for the addition of cyclohexene into the fuel on cell voltage

The cell voltage was gradually decreased as the addition of cyclohexene started. After about 200 hours the rate of decrease in cell voltage stabilized. It was almost the same level as that of extrapolated. In case of second addition, the behavior was similar to the first one. When the addition of cyclohexene was terminated after the test for about 800 hours, the cell voltage also recovered to a value at the level of extrapolated level.

The current-voltage characteristics (IV), and the cyclic voltammogram (CV) at the anode side, are shown in Fig. 5 and Fig. 6, respectively. Fig. 5 shows that there were hardly any changes in current-voltage relationship. Shown in Fig. 6, there were hardly any changes in H desorption peak that was observed in the range of about 80 - 300 mV vs. RHE. It has been confirmed that there were hardly any changes in the active surface area of the catalyst.

It was confirmed that when cyclohexene is added from the anode side, while the cell voltage is decreased, it recovers reversibly by terminating the addition of cyclohexene. Considering that the cell voltage drop depends on the concentration of cyclohexene, it is suggested that the cell voltage drop was caused by a decrease in the active surface area of the catalyst as a result of the inhibition of the electrode reaction by impurities.

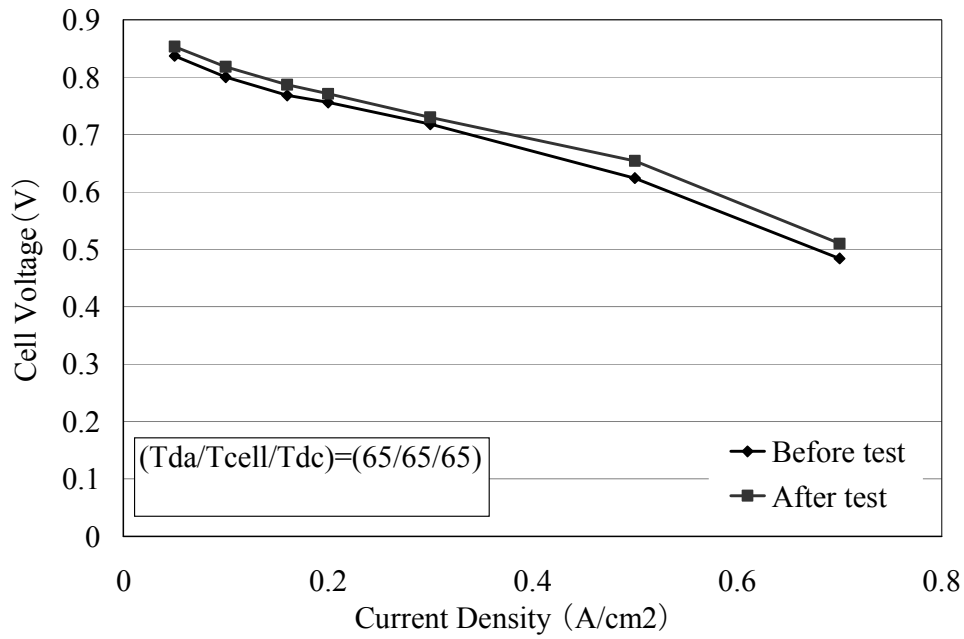


Fig. 5 The influence of cyclohexene on current-voltage curves

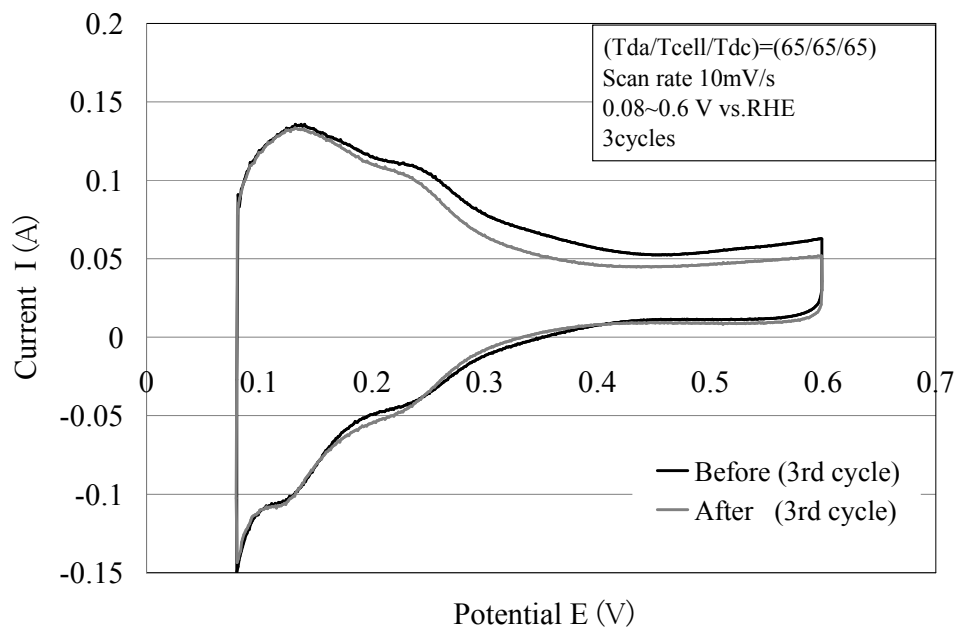


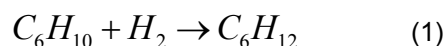
Fig. 6 CV curves before and after the addition of cyclohexene into the anode side

2.3.2 Study of a mechanism of influence of cyclohexene

In the test shown in Fig. 4, qualitative analysis was made to evaluate the composition of a gas exhausted from the cell during the addition test by gas chromatography. Cyclohexene and cyclohexane were detected. It is considered that this result was caused by the following reaction that occurred on

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the surface of the catalyst.



On the surface of catalyst at the anode side, it is considered that an inhibition of the electrode reaction on the anode catalyst by impurities like adsorption of cyclohexene might be occurred. It is suggested that cell voltage drop discussed in 2.3.1 might appear as a result of these inhibition. In order to evaluate an influence exerted on cell voltage by cyclohexane, an addition test of cyclohexane was carried out. The test result is shown in Fig. 7.

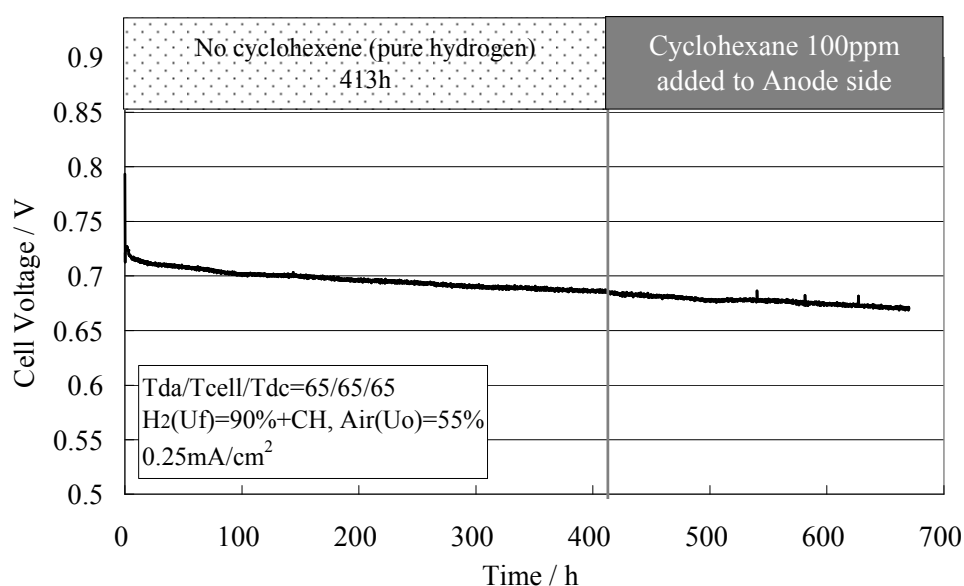


Fig. 7 The influence exerted on cell voltage by cyclohexene in hydrogen

As shown in Fig. 7, in the case of cyclohexane, there were hardly any influences on cell voltage. It is also reported that when n-hexane which is an alkane having a six-carbon skeleton like cyclohexane was added to the cell, the influence on cell voltage was very small and besides it was reversible^[7]. Although cyclohexane has a ring structure, it is considered that because cyclohexane is an alkane and has similar structure to n-hexane cyclohexane did not exert an influence similarly to n-hexane.

As mentioned above, the inhibition of the electrode reaction on the anode catalyst by impurities like adsorption of cyclohexene and cyclohexane and hydrogenation reaction of cyclohexene might be caused the cell voltage to be decreased. Considering that the rate of decrease in cell voltage was slow right after increasing the concentration and cyclohexene became cyclohexane in the cell, several reactions might occur on the catalyst could cause the cell voltage drop. Further studies on the mechanism are required.

2.3.3 Influence exerted on cell voltage by cyclohexene at the cathode side

Next, the effect of cyclohexene on the cell voltage at the cathode side was evaluated. This evaluation was made on assumption that the cyclohexene can move from anode to cathode. The concentration of cyclohexene in the air was set to 1, 5, 10 ppm, changing it at intervals of about 100 hours. After that the addition of cyclohexene was terminated and the behavior of cell voltage recovery was evaluated. The result is shown in Fig. 8.

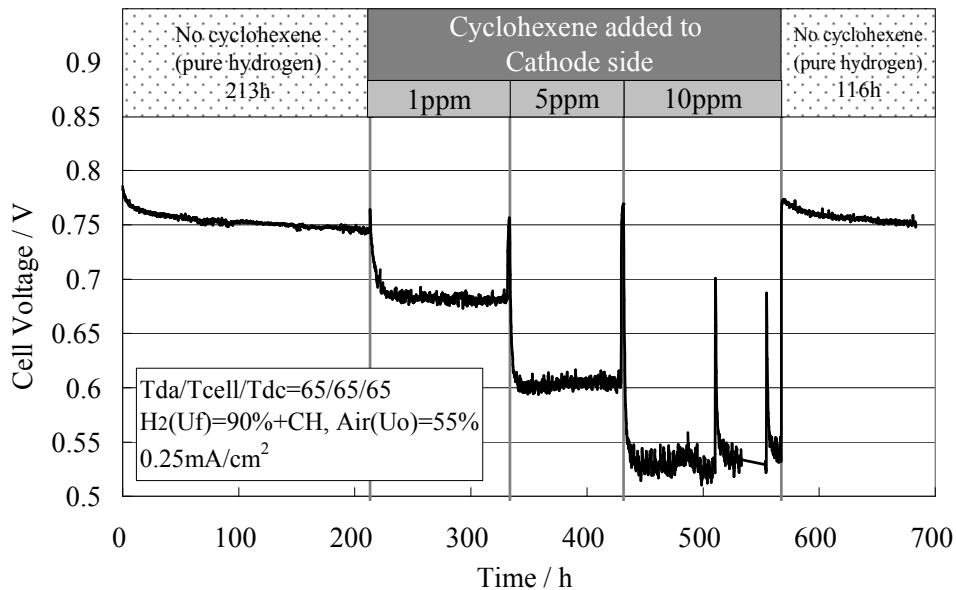


Fig. 8 The influence exerted on cell voltage by the addition of cyclohexene to the cathode side

When addition of cyclohexene was started, the cell voltage promptly decreased similar to the case of that at the anode side, and then it stabilized. The cell voltage drop became about 65 mV at a concentration of only 1 ppm, and was considerably greater than that at the anode side. The dependence on the concentration of cyclohexene was similar to that at the anode side, and the cell voltage drop became greater as the concentration increases. Cell voltage recovered completely directly after terminating the addition of cyclohexene as in the case of the anode side.

In order to analyze the state of the electrode, the measurement of CV at the cathode side was made, and the result was shown in Fig. 9.

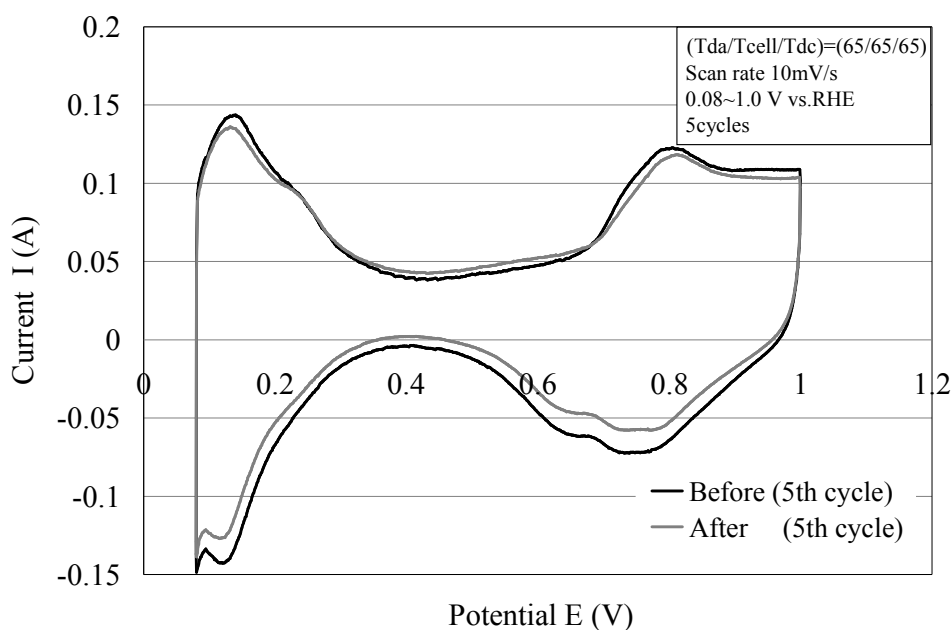


Fig. 9 CV curves before and after the addition of cyclohexene into the cathode side

Because hardly any differences were found in H desorption peak before and after the test in Fig. 9, it could be confirmed that hardly any changes occurred in the active surface area of the catalyst. It was confirmed that recovery occurred reversibly as a result of terminating the addition. Since hardly any hydrogen existed at the cathode side, the reaction shown in equation (1) did not occur. It is considered that the mechanism of the cell voltage drop was occurred by the decrease in active surface area resulting from the inhibition of the electrode reaction on the cathode catalyst by impurities like adsorption of cyclohexene at the cathode. The influence at the cathode is considerably greater than that at the anode because the oxygen reduction activity at the cathode is smaller than the hydrogen oxidation activity at the anode, the cathode is likely to be influenced by a small amount of cyclohexene, and that at the anode a change into cyclohexane having a smaller influence might be caused by the reaction in equation (1), and others.

2.4 Conclusions

We studied an influence on PEFC cell voltage by cyclohexene which is a prospect for an odorant to be added when supplying pure hydrogen.

Adverse effects by slightly contaminating cyclohexene in fuel hydrogen on fuel cell performance (IV curves or long-term degradation) were observed. The cell voltage drop was increased with the increase in concentration of cyclohexene. However, complete recovery in cell voltage was observed upon supplying pure hydrogen to the fuel cell. These results will be applicable to the design of pure hydrogen fuel cell co-generation systems in the future. In addition, it will contribute to the early

realization of a hydrogen economy.

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