Analyses on Declining Performance of PEMFC with Fuel Containing Impurities*

(Proposal of Analytical Methods Adopting Poisoning Prediction Formulas and Poisoning Estimation Coefficient)

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This paper covers our investigation into a decline in FC performance resulting from hydrogen fuel containing CO. Several investigations were conducted into the dependence of CO poisoning on types of catalyst using Pt and Pt-Ru alloy. The investigations are summarized as follows: 1) The poisoning prediction formulas and the poisoning estimation coefficient to predict and estimate the performance were derived theoretically. 2) The actual process of CO poisoning was scrutinized by focusing on adsorption of CO and desorption of CO₂ molecules, and changes of several polarizations caused by CO poisoning were estimated. 3) Investigations into the relationship between the CO concentration, operating pressure, operating temperature and the CO poisoning were carried out. If the FC was operated at a high CO concentration, no significant improvement could be expected when using increased pressure, and further, the effects of the operating temperature is almost the same for the two types of catalyst.

Key Words: Automobile, Alternative Energy, Catalyzer, Fuel Cell, Carbon Monoxide

1. Introduction

In recent years, the so-called environmental energy issue resulting from problems such as fossil fuel depletion, global warming, air pollution and acid rain etc. has been widely discussed. Due to this, there has been mounting pressure on the automobile industry to develop automobiles that are equipped with clean environmentally friendly power sources, which

can replace the conventional combustion engine⁽¹⁾, and fuel cell vehicles⁽²⁾ are presently attaining much attention as a potential replacement for combustion engine vehicles. This paper reports about the results of our analysis concerning the problem of a decline in the electricity generation performance of the fuel cell (poisoning), resulting from the use of hydrogen fuel containing CO⁽³⁾ in fuel cell vehicles. The specific details of our investigation were as follows.

1) Analytic methods that utilize poisoning estimation coefficients and poisoning prediction formulas were proposed.

2) The development mechanism of CO poisoning and polarization changes in the fuel cell were analyzed.

3) The dependency of CO poisoning on mixed CO concentration, operating pressure and operation temperature were investigated.

Further, in this investigation a variety of types of experimental and analytical tests were carried out on the Proton-exchange Membrane Fuel Cell

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(PEMFC)⁽⁴⁾, which has proven itself the most practically successful fuel cell for automobile use.

2. Experimental Apparatus for Testing the Proton-Exchange Membrane Fuel Cell

Figure 1 shows the PEMFC used in our research. This FC was installed within the characteristic evaluator (SOKKEN GT100) shown in Fig. 2, and various experimental investigations were carried out under the operation conditions shown in Table 1. As the PEM, a compound of a stretched porous membrane of polytetrafluoroethylene and an ion exchange resin was adopted. This PEM was placed in good contact with the catalytic layer at their connection interface, thus forming the membrane electrode assembly (MEA). In addition, a carbon-cross gas diffusion layer was provided at the backside.

3. Analysis of CO Poisoning

In this section, attention will be focused on CO,

Table 1 FC specifications and experimental conditions

Items	Specifications, Setting
Surface Area	10 cm ²
PEM	30 μ m
Catalyst	0.3 mg Pt/cm ² , 0.45 mg Pt-Ru/cm ²
Operating Pressure	1 bar (Atmospheric Pressure)~3 bar
Operating Temperature	30 $^{\circ}$ C~100 $^{\circ}$ C
Flow Rate	Fuel 500 cc/min, Air 2000 cc/min

Fig. 1 PEM fuel cell used for our investigations

Fig. 2 FC characteristic evaluator (SOKKEN GT100)

which is the predominant impurity within the constituents of hydrocarbon reformed fuel gas. Furthermore, the results of various experimental and analytical experiments that were carried out in order to ascertain the extent of the adverse effect of CO on the electricity generation performance of the FC are summarized.

3.1 Analysis concerning the development of CO poisoning

The PEMFC is an electric generator that utilizes a reverse water electrolysis process to generate electricity. In more specific terms, in the fuel electrode an electric current is generated when electrons are released when H₂ molecules are adsorbed onto the catalyst electrode. However, if CO impurity is contained within the fuel it begins to cover the surface of the catalyst electrode instead of the H₂, since the CO adsorbs more strongly. As a result of this, the dissociation reaction of the H₂ molecules that was originally intended to occur is impeded (Fig. 3). However, at the same time as CO molecules are adsorbed onto the surface of the electrode, they react with water vapor that has been supplied for humidification and are thus oxidized and desorbed in the form of CO₂ molecules. This eventually leads⁽⁵⁾ to the formation of a stable desorption equilibrium since the entire surface of the catalyst is not coated with CO molecules. Next, our fundamental experiment that was designed to analyze the specific details of the development of this poisoning, and its results, will be discussed. In the experiment, an FC that was in the midst of electricity generation using pure H₂ fuel, had CO injected into its fuel supply. Once a stable desorption equilibrium had been reached the injected CO supply was stopped, and the change in the electricity generation performance time when the CO supply stoppage took place was studied.

The test results are shown in Fig. 4. If it is assumed that CO is absorbed more strongly onto the catalyst than H₂, and thus at the time of adsorption CO directly collides with the electrode without being

Fig. 3 Principle of CO poisoning

interfered with by other substances, the formulas shown in Fig. 5 can be established for times at which CO is being injected into the fuel supply⁽⁶⁾.

$$dv/dt = kp(v_s - v) - cv = cv_s(v_e - v)/(v_s - v_e) \quad (1)$$

$$v = v_e(1 - e^{-c v_s t/(v_s - v_e)}) \quad (2)$$

$$kp(v_s - v_e) = cv_e \quad (3)$$

where, v : CO adsorption [mol], v_s : saturated adsorption amount [mol], v_e : CO equilibrium adsorption amount [mol], p : CO concentration [ppm], k : CO adsorption speed coefficient [1/(s·ppm)], c : CO oxidation desorption speed during CO saturated adsorption (CO_2 generation speed) [1/s]. Further, if it is assumed that the reduction in the current density J caused by poisoning is proportionally related to the adsorption amount of CO to the catalyst electrode, the following formula can be established.

$$J = J_0 - av = J_0 - J_e(1 - e^{-c v_s t/(v_s - v_e)}) \quad (4)$$

where, J_0 : Current generation when there is no poisoning [A], a : Proportionality constant [A/mol], J_e : Reduction in generated current resulting from poisoning (during stable equilibrium) [A]. Each coefficient was derived from the experimental values, and the analysis results that were obtained are shown within Fig. 4. The results of the analysis and the actual experiment had a relatively high degree of agreement.

As a result of this analytical and experimental investigation, the reversibility of the CO poisoning

Fig. 4 CO poisoning (CO: 100 ppm, 30°C, 0.5 V, 1 bar)

Fig. 5 Concept of the CO poisoning analysis

phenomenon and the rapidness of the reduction in generated current caused by CO mixing, and in contrast to this, the need for a time period for the generated current to recover etc., were clearly confirmed. Meanwhile, an overview of the change in electricity generation performance caused by CO poisoning can be presented, using the described analytical method for the CO adsorption and CO oxidation desorption mechanism.

3.2 Change in the polarization phenomena resulting from CO poisoning

Next, our investigation into changes in the FC polarization characteristics resulting from CO poisoning will be explained. The reduction in voltage during electricity generation, or in other words, the polarization E , can be broken down as shown in the following formula.

$$E = E_a + E_r + E_c \quad (5)$$

where, E_a : Activation polarization (corresponds to the electricity generation feedback energy) [V], E_r : Resistance polarization (corresponds to the electricity generation resistance) [V], E_c : Concentration polarization (corresponds to the reaction gas shortfall) [V]. Figure 6 shows the changes in these polarizations during non-poisoned and poisoned periods. In the experiment the Current Interruption Method (the circuit was broken 5 times/s, i.e. at 200 μs /time) was utilized for measurement. Further, a voltage ($V_0 - E_a$) in the figure which only considers activation polarization was estimated from the gradient of the experimental data (200 mA/cm² or less) for low output periods when generation of concentration polarization was not expected.

First, usage of the Pt Catalyst was observed. If the poisoned period (at 20 ppm) is compared with the non-poisoned period, the activation polarization is approximately 1.2 times greater in the former. This is because there is a drop in the effective reaction surface of the electrode for the H_2 dissociation reaction, caused by adsorption of CO onto the catalyst. If resistance polarization is focused on, a similar increase of about 1.2 times is also apparent. In this case, given that the resistance of the electronic conductors such as the pole plates and the separator etc. does not change, the change in resistance polarization is probably caused by a reduction in the conductivity of the hydrogen ions in the vicinity of where CO has been adsorbed onto the electrode⁽⁷⁾. Lastly, the concentration polarization increases markedly. This is presumed to be a result of the adsorbed CO electrons making the movement of the fuel H_2 electrons insufficient, which causes the number of H_2 electrons supplied to the surface of the catalyst to be inadequate⁽⁸⁾.

Next, comparative performance changes that occurred when using the Pt-Ru catalyst in the experiment will be considered. During poisoned periods (at 20 ppm) the activation polarization increased by a miniscule amount, but the resistance and concentration polarization barely changed at all. Therefore, it

(a) Using Pt catalyst (CO 0 ppm)

(b) Using Pt catalyst (CO 20 ppm)

(c) Using Pt-Ru catalyst (CO 0 ppm)

(d) Using Pt-Ru catalyst (CO 20 ppm)

Fig. 6 Changing of several polarizations caused by CO poisoning

can be inferred that the CO poisoning causes almost no adverse effect. Further, during the non-poisoned period when a Pt-Ru Catalyst was utilized, the activation polarization was significantly smaller than that observed when a Pt Catalyst was used. This was presumed to be a result of the degree of activity of the dissociation reaction being different, since different amounts of the catalysts were used.

3.3 Dependence of CO poisoning on mixing concentration and the proposal of a poisoning estimation formula and a poisoning coefficient

In this section the dependency of the fall in electricity generation performance on the mixing concentration of CO in H₂ fuel is examined. The results of our experiment are shown in Fig. 7.

For the investigation, the following poisoning estimation formulas were employed, as well as the experiment results. If $v_{e(\text{CO})} + v_{e(\text{H}_2)} = v_s$ is assumed as the speed equilibrium formula of Eq.(3), then the following formulas can be established.

$$kp v_{e(\text{H}_2)} = c(v_s - v_{e(\text{H}_2)}) \quad (6)$$

$$v_{e(\text{H}_2)} = v_s / (Kp + 1) \quad (7)$$

$$K = k/c \quad (8)$$

where, $v_{e(\text{CO})}$: CO equilibrium adsorption amount [mol], $v_{e(\text{H}_2)}$: H₂ equilibrium adsorption amount [mol]. Further, if it is assumed that the current density J is proportional to the adsorption amount, the following poisoning estimation formula can be estab-

(a) Using Pt catalyst

(b) Using Pt-Ru catalyst

Fig. 7 Dependence of CO concentration on CO poisoning (70°C; 1 bar)

lished.

$$J = a_{(\text{H}_2)} v_{\text{e}(\text{H}_2)} = a_{(\text{H}_2)} v_s / (Kp + 1) \quad (9)$$

where, $a_{(\text{H}_2)}$: Proportionality constant between the hydrogen adsorption amount and current amount generated [A/mol]. In this formula, the value of K indicates the extent of the poisoning. Hereafter, this shall be referred to as the poisoning coefficient. By comparing different poisoning coefficient values, it was possible to attain a quantitative comparison of the extent of poisoning that occurred, when various gases with different impurity levels or various catalyst electrodes were used under constant operating temperature conditions^{(9),(10)}.

Each constant of the poisoning estimation formula was derived from the 0 ppm and 100 ppm CO injection concentration experiment values. Estimated calculations of the performance of the catalysts if CO were injected at 20 ppm and 50 ppm were made, as shown in Fig. 7. Further, the characteristic performance curve was obtained for each fixed voltage value by calculation using Eq. (9). It was confirmed that the experimental values and the analysis results were almost exactly the same for each catalyst.

As a result of the experiment and analysis, it is clearly apparent that there is an extreme worsening in electricity generation performance when a Pt Catalyst is used with CO mixed in its fuel at 50 to 100 ppm, which is the concentration of CO that is expected to be generated from present-day reformers. However, this problem is almost completely solved if a Pt-Ru catalyst is utilized instead. This is probably because the Ru on the catalyst surface promotes the oxidation and desorption of the CO that has been adsorbed onto the Pt⁽⁵⁾. Further, the poisoning coefficient for when the Pt Catalyst ($K_{\text{Pt}} = 5.6 \times 10^{-2} [1/\text{ppm}]$) is used is calculated to be about 70 times the poisoning coefficient when the Pt-Ru Catalyst ($K_{\text{Pt-Ru}} = 8.0 \times 10^{-4} [1/\text{ppm}]$) is used. This in effect means that if using the Pt-Ru Catalyst instead of the Pt Catalyst, the same level of poisoning will occur when CO is injected at a concentration that is about 70 times greater than the concentration used in the Pt Catalyst.

3.4 Analysis of the dependence of poisoning on operating pressure

By increasing the operating pressure of the FC, the electricity generation output is improved, mainly as a result of an improvement in the activation polarization of the air electrode⁽¹¹⁾. As a result of this, pressurized operation is often used in FC systems for automobiles as well, so long as it does not cause loss of electric power for accessories such as air blowers etc.⁽¹²⁾ In this section the dependence of poisoning on operating pressure will be examined.

Figure 8 shows the results of an experiment

concerning electricity generation performance of the FC when operated with H_2 fuel with injected CO, under normal and increased pressure (3 bar) conditions. Once again, the analysis results derived using the poisoning estimation formula are shown. In the case of using pure H_2 fuel the generation performance was dramatically improved by the pressure increase. However in contrast to this, when the FC was operated under CO poisoned conditions, and particularly in the high CO concentration range, a limited performance improvement could be expected as a result of the pressure increase regardless of which catalyst was used. This was because the amount of CO adsorbed onto the catalyst also increased, even though the dissociation reaction was promoted by high pressure operation. In the case of the poisoning coefficient value, it increased by approximately 2 times for the Pt Catalyst and 4 times for the Pt-Ru Catalyst, when high pressure operating conditions were compared with normal ones. As observed before, performance improvement is restrained by the adverse influence of the poisoning.

3.5 Analysis of the dependence of poisoning on operating temperature

Next, the dependence of poisoning on operating temperature will be examined. Figure 9 shows the results of an experiment concerning electricity generation performance under various temperature conditions. When operating with a pure H_2 fuel supply the

(a) Using Pt catalyst

(b) Using Pt-Ru catalyst

Fig. 8 Dependence of operating pressure on CO poisoning (70°C)

performance peak occurs in the vicinity of 90°C. This is because the PEMFC the optimum operating temperature is based on the temperature dependence of the electricity generation performance and membrane resistance. In more concrete terms, the generation reaction time speeds up as the temperature rises. However, with regard to membrane resistance, fuel gas humidification does not take place sufficiently as the temperature rises and thus comparative humidity does not reach 100%. This causes moisture desorption from the membrane to occur and the membrane resistance to increase. On the other hand, when CO is mixed within the fuel, the electricity generation performance is improved as the temperature rises. This is because the level of poisoning decreases as the temperature rises because CO adsorption is an exothermic reaction.

As a result of the above investigation, it is obvious that increasing the operating temperature can significantly reduce the problem of CO poisoning. In line with this, operation should take place at high temperatures to the extent that this does not lead to membrane management difficulties. Further, it is also clearly apparent that the poisoning prevention effect when a Pt-Ru Catalyst is used is most prominent during low temperature operation.

The results of our experiment concerning the dependence of the development of poisoning on temperature are shown in Fig. 10. When a Pt-Ru Catalyst is used, generation output improves swiftly after the injected CO supply is stopped in comparison to a Pt Catalyst. This is true for both high operating temperatures and low operating temperatures. Accordingly, when a Pt-Ru Catalyst is used, swift performance recovery is possible from a high concentration poisoned state at low temperatures. This characteristic can be expected to be beneficially utilized at automobile starting times when the FC has not sufficiently warmed up, and when high concentrations of CO are discharged from the reformer.

4. Conclusion

The results obtained from this research can be summarized as follows.

A) A poisoning estimation formula has been proposed that focus attention on adsorption of CO onto the catalyst electrode and oxidation dissociation. The proposed estimation formula can estimate electricity generation performance, when the concentrations of impurities mixed within fuel are changed discretionarily under constant operating temperature conditions. This formula was applied to analysis once its validity had been clearly shown through comparison with experimental results.

(a) Using Pt catalyst (CO 0 ppm)

(b) Using Pt catalyst (CO 100 ppm)

(c) Using Pt-Ru catalyst (CO 0 ppm)

(d) Using Pt-Ru catalyst (CO 100 ppm)

Fig. 9 Dependence of operating temperature on CO poisoning

(a) Operating temperature 30°C

(b) Operating temperature 70°C

Fig. 10 CO poisoning (CO: 100 ppm, 0.5 V, 1 bar)

B) A poisoning coefficient concept was proposed that allows quantitative comparison of the extent of poisoning under fixed operating temperature conditions when various gases with impurities and various catalyst electrodes are utilized, and was then applied to our analysis.

C) With regard to changes in the polarization characteristics of the FC caused by poisoning, it has been made fully clear that when the Pt Catalyst is operated under poisoned conditions as compared with non-poisoned ones, there is a slight reduction in activation polarization and resistance polarization, and a radical increase in concentration polarization. In the case of the Pt-Ru Catalyst, it has become apparent that there is a slight increase in the level of activation polarization, but that resistance polarization and concentration polarization barely change at all.

D) At times when a high concentration of CO is mixed within the fuel, it is now clearly evident that there is no significant increase in performance caused by an increase in operating pressure, regardless of whether the Pt Catalyst or the Pt-Ru Catalyst is used. This is presumed to be a result of the fact that when the pressure is increased, the dissociation reaction is encouraged, but simultaneously the amount of CO

adsorbed onto the electrode of the catalyst also rises.

E) It has been made transparent that increasing the operating temperature can significantly reduce the CO poisoning problem. Further, the poisoning reduction effect achieved when utilizing the Pt-Ru Catalyst, not only comes into effect when operating at normal temperature ranges, but is also effective at times of low temperature.

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