



# Adsorption behavior of low concentration carbon monoxide on polymer electrolyte fuel cell anodes for automotive applications



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## HIGHLIGHTS

- CO, CO<sub>2</sub> and O<sub>2</sub> in the anode exhaust were measured during the PEFC operation.
- CO coverage was estimated from gas analysis and CO stripping voltammetry.
- The CO coverage at low CO concentration followed a Temkin-type isotherm.
- The CO coverage was 0.6 at 0.2 ppm CO and 0.11 mg cm<sup>-2</sup> anode loading at 60 °C.
- Permeated O<sub>2</sub> should have an important role for CO oxidation at low CO concentration.

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## ABSTRACT

The adsorption behavior of CO on the anode around the concentration of 0.2 ppm allowed by ISO 14687-2 is investigated in polymer electrolyte fuel cells (PEFCs). CO and CO<sub>2</sub> concentrations in the anode exhaust are measured during the operation of a JARI standard single cell at 60 °C cell temperature and 1000 mA cm<sup>-2</sup> current density. CO coverage is estimated from the gas analysis and CO stripping voltammetry. The cell voltage decrease as a result of 0.2 ppm CO is 29 mV and the CO coverage is 0.6 at the steady state with 0.11 mg cm<sup>-2</sup> of anode platinum loading. The CO coverage as a function of CO concentration approximately follows a Temkin-type isotherm. Oxygen permeated to the anode through a membrane is also measured during fuel cell operation. The exhaust velocity of oxygen from the anode was shown to be much higher than the CO supply velocity. Permeated oxygen should play an important role in CO oxidation under low CO concentration conditions.

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## 1. Introduction

Polymer electrolyte fuel cells (PEFCs) are promising power devices for stationary, portable and transportation applications because of their high power density and efficiency. In particular, fuel cell vehicles (FCVs) are desirable because of the advantage of lower pollution emissions than internal combustion engine vehicles, and they have longer cruising distances than battery electric vehicles. Development and establishment of the hydrogen infrastructure is also in progress for the widespread use of FCVs.

At present, most hydrogen is produced by steam reforming from

hydrocarbons [1,2]. In the case of methane, the steam reforming is



After the steam reforming, carbon monoxide (CO) in the reformat gas is removed by the water gas shift reaction in Equation (2) and purified by pressure-swing adsorption or CO selective oxidation in Equation (3):



The CO concentration in the reformat gas after those reactions is reduced to a level of 10 ppm. Then, the hydrogen gas for the fuel cell is obtained by the separation of CO and other impurities in the

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pressure-swing adsorption process. However, a trace amount of impurities may remain in the hydrogen obtained as above. If the hydrogen purity is inadequate, the impurities may decrease the fuel cell's performance. On the other hand, excessively high hydrogen purity will lead to an increase in the hydrogen production cost. Therefore, a hydrogen quality specification for FCVs was discussed at ISO/TC197/WG12, which is the working group on hydrogen fuel specification, and was issued as an international standard as ISO 14687-2 in 2012 [3]. The allowable concentration of impurities in hydrogen fuel was specified in consideration of the effect of impurities on single cell performance or degradation of the constituent material. Methods for cell performance recovery after poisoning, analytical methods and accumulation behavior in the hydrogen circulation system were also considered [4]. This international standard applies to the early stages of commercial FCVs. Fuel cell cost reduction will be accelerated with the progress of technical development of fuel cell components, such as lowering of the platinum loading of electrocatalysts [5,6] and thinning of the electrolyte membrane. Preparation for the revision of the specification for hydrogen fuel is under way, looking ahead to the widespread usage stage.

Among the impurities specified in the standard, CO is known as having one of the greatest potentials to decrease fuel cell performance. In addition, a CO concentration that was almost the same as the upper limit of the CO standard has been reported at a hydrogen station [7,8]. So, the allowable concentration of CO is still an important subject for discussion for the revision of the hydrogen fuel specification.

There are many reports on the effect of CO poisoning on the performance of PEFCs [5,6,9–28] and on methods to decrease CO poisoning, such as by Pt–Ru electrocatalysts [5,9–15] and air-bleed systems [16–20] in PEFCs. However, application of these anti-poisoning techniques is difficult for FCVs because the Pt–Ru electrocatalyst has a low tolerance for sulfur-containing impurities [9], and the air bleed should cause nitrogen accumulation in the hydrogen circulation system of the FCVs, or membrane degradation by the formation of H<sub>2</sub>O<sub>2</sub> in the anode potential range [30]. Consequently, the evaluation of CO at low concentration with low anode platinum loadings is necessary for a discussion of the hydrogen fuel specification for the FCVs.

Gas emission behaviors when a relatively low concentration of CO is added to the fuel cell have been reported in the literature [6,24,25]. However, the influence of CO has not been well understood because the change of CO coverage during the PEFC operation was not clear. To discuss the allowable concentration of CO, which considers the MEA specification and the operating conditions with the widespread use of FCVs, it is important to understand the basic phenomena, such as the relationship between CO coverage and performance degradation of the PEFC.

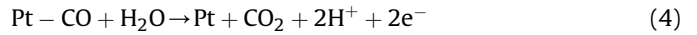
In addition, permeated oxygen from the cathode would react with hydrogen or CO on the anode electrocatalyst. If permeated oxygen exists in the anode exhaust, oxygen will accumulate in the hydrogen circulation system of the FCVs, and subsequently it will make a possible contribution to mitigating the effect of CO, as in air-bleed systems [16–22]. However, oxygen concentration in the anode exhaust has not been reported.

In this study, the adsorption behavior of CO on the anode during PEFC operation has been investigated to understand the progress of CO poisoning near the upper limit of ISO 14687-2 and recovery by high-purity hydrogen. Both CO and CO<sub>2</sub> concentrations in the PEFC exhaust were measured to evaluate the carbon balance of CO in the supplied hydrogen fuel. The oxygen concentration in the anode exhaust was also measured to evaluate the permeated oxygen content from the cathode.

## 2. Theoretical

In general, two types of bonding for CO adsorption are known on the platinum surface, linear and bridge bonds. The linear-bonded CO occupies one platinum site, while the bridge-bonded CO occupies two sites. Igarashi et al. reported that the type of CO bonding on Pt sites was dependent on the CO coverage, and that linear-bonded CO is dominant near full coverage [26]. To estimate the CO coverage in a single cell under operation with hydrogen containing a low concentration of CO, the two possible CO coverage scenarios, which are only linear-bonded CO ( $\theta_L$ ) and both linear- and bridge-bonded CO ( $\theta_{L+B}$ ), are considered here.

The CO coverage is estimated by determination of the two types of CO adsorption. One is measured by CO stripping voltammetry and the other is measured by anode exhaust analysis during cell operation. In CO stripping voltammetry, if the platinum catalyst is exposed to a high concentration of CO, linear-bonded CO dominates and the CO coverage reaches almost 1.0 [26]. Then the electrochemical oxidation of CO is expressed by the following equation.



The amount of CO adsorption  $n$  (mol) is estimated using the CO oxidation charge  $Q_{\text{CO}}$  (C) and geometric electrode area  $A_{\text{Cell}}$  (cm<sup>2</sup>) as follows:

$$n = \frac{Q_{\text{CO}} A_{\text{Cell}}}{2F}, \quad (5)$$

where  $F$  is the Faraday constant ( $= 9.65 \times 10^4 \text{ C mol}^{-1}$ ). The whole platinum surface area  $S_{\text{CO}}$  (m<sup>2</sup>) is represented by the charge needed to strip a monolayer of CO on platinum, 420  $\mu\text{C cm}^{-2}$ :

$$S_{\text{CO}} = \frac{Q_{\text{CO}} A_{\text{Cell}}}{420}. \quad (6)$$

The CO and CO<sub>2</sub> concentrations in the anode exhaust of a single cell were measured to estimate the amount of CO adsorption. The CO exhaust velocity  $v_{\text{CO,out},t}$  (mol h<sup>-1</sup>) and the CO<sub>2</sub> exhaust velocity  $v_{\text{CO}_2,\text{out},t}$  (mol h<sup>-1</sup>) at time  $t$  (h) can be represented as follows:

$$v_{\text{CO,out},t} = \left(1 - \frac{1}{S_f}\right) \frac{C_{\text{CO,out},t} F_{\text{H}_2}}{V_m}, \quad (7)$$

$$v_{\text{CO}_2,\text{out},t} = \left(1 - \frac{1}{S_f}\right) \frac{C_{\text{CO}_2,\text{out},t} F_{\text{H}_2}}{V_m} - v_{\text{CO}_2,\text{b},t}, \quad (8)$$

where  $C_{\text{CO,out},t}$  (ppm) and  $C_{\text{CO}_2,\text{out},t}$  (ppm) are the cell outlet CO and CO<sub>2</sub> concentrations at time  $t$  (h), respectively.  $S_f$ ,  $F_{\text{H}_2}$  (L h<sup>-1</sup>),  $V_m$  ( $= 22.4 \text{ L mol}^{-1}$ ) and  $v_{\text{CO}_2,\text{b},t}$  are the anode stoichiometry, fuel flow rate, mole volume and CO<sub>2</sub> exhaust velocity baseline, respectively.

All CO supplied to the anode is thought to be exhausted as CO or CO<sub>2</sub> at the steady state. Here, the CO and CO<sub>2</sub> exhaust velocity at the steady state are defined as  $v_{\text{CO,out},s}$  (mol h<sup>-1</sup>) and  $v_{\text{CO}_2,\text{out},s}$  (mol h<sup>-1</sup>), respectively. Therefore, the CO adsorption velocity  $v_{\text{CO,cell},t}$  (mol h<sup>-1</sup>) at time  $t$  (h) can be represented as follows:

$$v_{\text{CO,cell},t} = (v_{\text{CO,out},s} + v_{\text{CO}_2,\text{out},s}) - (v_{\text{CO,out},t} + v_{\text{CO}_2,\text{out},t}). \quad (9)$$

Then, the cumulative CO adsorption amount per platinum surface area  $q_{\text{CO}}$  (mol m<sup>-2</sup>) is

$$q_{\text{CO}} = \frac{1}{S_{\text{CO}}} \int_0^t (v_{\text{CO,cell},t}) dt. \quad (10)$$

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