Determination with a Genetic Algorithm of Reactant Coverages on H₂/H₂O Electrodes Based on Electrochemical Kinetics Under Reversible SOFC/EC Operation

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Abstract

A scheme to quantify surface coverages of reactants at triple phase boundary (TPB) by electrochemical measurements was constructed to evaluate the electrode performance of solid oxide fuel cells and electrolysis cells (SOFC/EC). The developments of electrode requires that the intrinsic properties of materials separated from the effect of geometric structure of the electrode. The proposed reaction model at TPB of H₂/H₂O electrodes is composed of competitive adsorptions and Langmure-type surface reactions under the relationship between oxygen activity (aO) and the electrode potential. To determine the reaction constant (ka) and four adsorption equilibrium constants at TPB (KH, KH₂O, KO and KOH), a machine learning approach with a genetic algorithm as an optimization method and the experimental data of reversible SOFC/ECs with different H₂/H₂O partial pressures as the learning data was developed. As a result, even though all experimental curves of the current density vs. aO in SOFC operation were fitted by numerous sets of the five constants, the coverages under different conditions could be uniquely determined. Results suggest that TPB at 900°C was almost vacant with a small amount of H₂O in SOEC operation, and was not vacant and the OH coverage increased with increasing aO in SOFC operation.

Keywords: Competitive Adsorption, Genetic Algorithm, Reaction Kinetics, Solid Oxide Electrolysis Cell, Solid Oxide Fuel Cell, Surface Coverage, Triple Phase Boundary

1 Introduction

Expectation for solid oxide fuel cells/electrolysis cells (SOFC/ECs) are increasing with the increasing demand for large-scale, low cost energy storage [1–3]. Although it is necessary to reduce the SOFC/EC cost, improving the cell characteristics, that is, improving the power density for SOFCs and the current density at the heat neutral point for ECs, is directly linked to the cost reduction of the entire system [4–8]. In addition, the cost can be reduced by the integrated type that utilizes reversible operation [4, 5]. On the other hand, SOFCs have been extensively researched from materials to devices, however electrode development related to SOECs is in progress, and most materials and devices are based on SOFCs [5–11]. And not only top performance but also characteristics, such as characteristics with a wide range of loads, followability...

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ity and efficiency during transient operation are important, in order to respond to fluctuating power sources and fluctuating demand derived from renewable energy. Therefore, it is crucial to evaluate the SOFC/EC electrodes and establish a comprehensive kinetics model for quantitative electrode reactions, especially surface chemical/electrochemical reactions, toward new development.

One of the challenges in SOFC/EC material development is that it is difficult to directly analyze and evaluate the state of the reaction field in the oxide/metal composite at high temperature. It is important to clarify the state of the electrode surface, because the electrode kinetics is directly linked to the coverage of reactive species or their relative values on the electrode surface, especially the triple phase boundary (TPB) [12–22]. However, it is difficult to separate the effect of the porous structure with three dimensional TPB from the intrinsic characteristics of the materials. In Gd-doped CeO$_2$ with fluorite structure [23, 24] and ion conductive oxides with perovskite structure, especially in proton conductive oxides, such as BaCe$_{0.8}$Y$_{0.2}$O$_{3-δ}$ [25], SrZr$_{1-x}$Y$_x$O$_{3-δ}$, SrZr$_{1-x}$Yb$_x$O$_{3-δ}$ [26], SrCe$_{1-x}$Yb$_x$O$_{3-δ}$ [27], and Pr-Doped Ba$_2$In$_x$O$_y$ [28], the amount of oxygen vacancy depends on the surface gas atmosphere such as oxygen partial pressure. Thus, not only the surface coverages of reactants but also the interior bulk properties change under a vacuum condition and/or different gas atmospheres, thus making it difficult to detect the surface coverage independently. Although certain in situ spectroscopic measurement technologies, such as Raman spectroscopy [29], have enabled to detect NiO in the cermet electrode or ambient pressure. X-ray photoelectron spectroscopy (XPS) [30] have enabled measurement of the oxidized state of the oxide material surface, but it is difficult to observe the coverage of chemical species on the electrode surface. Also, a method for quantifying the adsorbed species (H, OH, etc.) at the TPB has not yet been established. Determining the state of chemical species at the TPB requires the development of a comprehensive approach based on electrochemical evaluation of electrodes.

Hydrogen oxidation kinetics on SOFC hydrogen electrodes and water reduction on SOEC water electrodes have been extensively discussed, based on a pair of reversible reactions at TPB and developed the reaction models including the surface coverage of the reactants as the parameters [12–22]. The configurations of the anode were Ni pattern electrodes on YSZ to define the length of TPB [12, 18, 22] or the porous cermet electrode as the commercial cells [13–16, 19]. Mizusaki et al. proposed a reaction kinetics model that assumed equilibrium of the oxide ion in the electrolyte and the oxygen adsorbent at TPB, and assumed local equilibrium of O$_2^-$, O$_2$, and e$^-$ at YSZ in the electrode [12]. Under these equilibrium assumptions, the oxygen activity ($a_{O_2}$) and the surface coverage of oxygen ($θ_O$) correspond to the electrode potential. This reaction model was discussed in terms of the reaction order (i.e., current density ($i$) vs. $a_{O_2}$ and electrode interface conductivity vs. partial pressure of H$_2$ or H$_2$O ($P_{H_2}$, $P_{H_2O}$) measured via experiments on the pattern anode. The coverages of reactants on the active site of TPB were assumed to be the coverage of the vacancy ($θ_i$) as ~1. Based on those assumptions, Wen et al. described the relationship between $i$ and the anode overpotential with the adsorption/desorption equilibrium and the surface chemistry under the assumption of $θ_i$ ~1, and suggested that the overpotential can be reduced by keeping $P_{H_2O}$ at an appropriate level [13]. Jiang et al. proposed a reaction model in which adsorbed oxygen on Ni acts as an effective adsorption site of hydrogen based on the effect of $P_{H_2O}$ on the anode overpotential measured by AC impedance measurement at low $P_{H_2O}$ [14]. The relationship between $P_{H_2O}$, $P_{H_2}$ and the exchange current density ($i_0$) in the Butler-Volmer equation was discussed and the existence of optimum $P_{H_2O}$ to minimize the overpotential was suggested [15].

On the other hand, even though numerous researchers have evaluated the reaction on Ni/YSZ electrodes, the relationship between $P_{H_2}$ or $P_{H_2O}$ and the electrode performances have varied even at same operating conditions of $P_{H_2}$, $P_{H_2O}$ and temperature [16]. Thus, Ihara et al. proposed a comprehensive reaction model of SOFC/EC reaction using Langmuir competitive adsorption that enables description of such varied effect of $P_{H_2}$/$P_{H_2O}$ on DC polarization properties and on AC impedance properties [16]. In an actual SOFC electrode, the surface state at TPB, such as the crystal phase of each material, can depend on the source materials and/or preparation process. As a result, the properties of DC polarization and/or AC impedance at different $P_{H_2}/P_{H_2O}$ ratio can be varied depending on the surface coverage of reactants at TPB. Thus, by assuming local equilibrium in the electrolyte and equilibrium with competitive adsorption at TPB, the proposed model is based on a Langmuir-type kinetics equation of SOFC/EC which are both higher and lower than the equilibrium potential [16]. Variation in the reaction order of $a_{O_2}$, $P_{H_2}$, and $P_{O_2}$ to $i$ represents the coverage ratio of chemical reactants vs. $θ_i$. By using the model, the kinetics constant ($k$), which depends on the geometric structure of the porous electrode, and the equilibrium constant ($K$), which is intrinsic properties of the material surface, can be separately discussed. By applying the model to FC/EC data under a wide range of $a_{O_2}$, $P_{H_2}$, and $P_{H_2O}$, the relationship between the FC/EC conditions and the coverage of the reactants can be directly determined.

Based on those investigations, a number of studies have proposed anode reaction models [17–22]. From the viewpoint of determining the surface coverage of the reactants of the electrode by data fitting, these models can be organized based on the following four factors: (i) rate determining reaction; (ii) assumption of the local equilibrium of oxygen, oxide ion and electron in the electrolyte, and/or the equilibrium between oxide ion in the electrolyte and the oxygen adsorbents on the active site, both of which correspond to the relationship among the oxygen coverage, oxygen activity and the anode potential; (iii) assumption of Langmuir-type reaction based on competitive adsorption on the electrode surface, and thus enables calculation of the coverage; and (iv) approximations in the model equations.

Bieberle et al. proposed a reaction model composed of six reversible processes at TPB, namely, the charge transfer reac-
tion of $\text{O}_2^- + V_{\text{ad},\text{Ni}} \rightarrow O_{\text{ad},\text{Ni}} + V_{\text{O}},^{2-} + 2e^-$ (where $X_{\text{ad},\text{Ni}}$ is the adsorbent of the reactant, $V_{\text{ad},\text{Ni}}$ is the vacancy of the adsorbent on Ni active site, and $O_{\text{ad}}$ and $V_{\text{O}},^{2-}$ are, respectively, the lattice oxygen and oxygen vacancy in the electrolyte bulk), adsorption and desorption of $\text{H}_2$ and $\text{H}_2\text{O}$, and three surface reactions including $O_{\text{ad}} + H_{\text{ad}} \rightarrow OH_{\text{ad}} + V_{\text{ad}}$, $OH_{\text{ad}} + H_{\text{ad}} \rightarrow H_2O_{\text{ad}} + V_{\text{ad}}$ and $2OH_{\text{ad}} \rightarrow O_{\text{ad}} + H_2O_{\text{ad}}$ [17, 18]. The model uses the mass balance equation with $\theta_{\text{ad},\text{Ni}}$, $\theta_{\text{OH},\text{ad}}$, and $\theta_{\text{H}_2\text{O},\text{ad}}$ at TPB and numerically calculates those $\theta$ at the steady state. In contrast to the models in [12, 13, 16], in this model the competitive adsorption to occupy the limited number of active sites by the reactants (iii) was not investigated, nor was the local equilibrium of oxygen in the electrolyte, oxide ion and electron assumed, and the ratio of oxygen vacancy in the electrolyte (ii) was kept constant, namely, independent of the anode potential, and thus the coverage of each reactant did not depend on the potential of the electrode.

Zhu et al. proposed a reaction model of the $\text{H}_2$/$\text{H}_2\text{O}$ reaction assuming (i) a charge transfer reaction of $H_{\text{ad}}$ on Ni and $OH^- + YSZ$ across TPB as the rate limiting step under the adsorption equilibrium of $H$ on Ni, adsorption equilibrium of $H_2\text{O}$ on YSZ, equilibrium between $O_{\text{ad}}$ and $O^2-$ on YSZ surface, and quasi-equilibrium of the reversible reaction between $H_{\text{ad}}$ on Ni and $O^2-$ on YSZ across TPB [19]. This reaction model was constructed using the coverage of each reactant, and then simplified into the Butler-Volmer equation (iv) under the assumption that the active site of YSZ was almost completely covered with $O^2-$ [19]. Then, in order to understand the reaction mechanism of a $H_2$/$H_2\text{O}$ electrode, the group applied the model to SOFC/EC data on the patterned electrode reported by Mizusaki et al. [12] under various $P_{\text{H}_2}$ and $P_{\text{H}_2\text{O}}$ and determined the symmetric factor ($\beta$) in the Butler-Volmer equation as the comprehensive constant of the reaction [20]. The model equation was a polynomial with the coverage of multiple species $x$ ($\theta_x$) under the assumption of competitive adsorption (iii). Although neither the local equilibrium of the oxygen, oxide ion and electron in the electrolyte nor equilibrium between the oxide ion and the surface oxygen adsorbent were assumed (ii), the coverage of each species depends on the activation potential in the Butler-Volmer equation, and thus the coverage of each reactant can be determined by appropriate data fitting. In those works, fitting of the comprehensive Butler-Volmer equation and the current-overpotential curves under the assumption that $\theta_{\text{O}_2^-,-YSZ} = 1$ enabled the coverage of only $OH^-$ on YSZ to be determined.

Bessler et al. developed a scheme to simulate the SOFC reaction by generalizing the approach of Biebler et al. [17]. In this scheme, the rate equation of each specific process in an SOFC, such as gas flow, adsorption/desorption of reactants, surface diffusion and chemical/electrochemical reactions and the ion transport were prepared, the equations of the total mass and charge balance with a general electrochemical equation were constructed, and the steady state at TPB were derived numerically [21]. Furthermore, the rate constant of each process without the charge transfer reaction was not determined by fitting the experimental data but by substituting the value obtained from literature as a physical property [31-34]. Based on this scheme, Volger et al. simultaneously investigated multiple possible reaction pathways [22]. A reaction pathway including one or two charge transfer processes was assumed, and then previously reported values were substituted for the values of the kinetics constants of other processes, such as adsorption/desorption [31–34], or chemical reaction on Ni or on YSZ [31, 32], including their temperature dependence. By applying this model [21] to the AC impedance properties under different $P_{\text{H}_2}$, $P_{\text{H}_2\text{O}}$ and temperature [18], the suggested reaction pathway which sufficiently describes the data includes the charge transfer reaction of $H_{\text{ad}}$ on Ni and $O^2-$ on YSZ or $H_{\text{ad}}$ on Ni and $OH^-$ on YSZ across TPB, and the rate determining step was assumed to be one of these reactions (i). By these methods, the steady state coverage of the reactants, including the vacant site, can be determined by calculating the rate constant of charge transfer by data fitting, but the specific values strongly depend both on the set of kinetics constant and the equilibrium constants obtained from literature and on the reliability of those parameters under actual SOFC/EC conditions. Also, as the model suggested by Biebler et al. [17], the local equilibrium of the oxygen, oxide ion and electron in the electrolyte and the equilibrium between the oxide ion and the surface oxygen adsorbent were not assumed (ii), and the ratio of oxygen vacancy in the electrolyte was assumed to be constant and thus independent of the electrode potential. Thus, the coverage of each reactant and the electrode potential were the independent of each other.

Thus, in order to develop the scheme to evaluate the chemical characteristics of the electrode materials by quantitatively determining the coverages of reactants at TPB, to select and/or establish the appropriate reaction model is required. Also, to apply any model to quantify the state of chemical species at TPB, sufficient set of experimental data and the appropriate multiple regression method are necessary. However, because both of them are not sufficient, although many of the proposed reaction models work as the method to understand the reaction mechanism on the electrodes, the chemical properties at TPB in the electrode have not been quantitatively determined. Although the number of studies focusing on the hydrogen generation reaction of SOEC based on the discussion of SOFC reaction models is increasing [7–10, 35–37], the comprehensive understanding of SOFC/EC reaction to determine the electrode properties with applying the knowledge of the SOFC models are still ongoing. Thus, in order to quantitatively understand the reaction kinetics of SOFC/EC and to enhance the development of the electrode performance, it is necessary to determine the chemical characteristics, such as surface coverage. In order to establish the scheme, all of the three components are required as (i) to establish the appropriate electrochemical model based on the existed SOFC reaction models, (ii) to develop the procedure for the data fitting of the multiple variables to the experimental data, and (iii) to obtain series of the sufficient number of experimental data to determine and validate the variables.
Technology is needed for optimizing the multiple variables and to efficiently obtain the global optimum by fitting the reaction model with experimental data. Recently, machine-learning technologies are rapidly developing and have been widely applied in the research field, such as the multiple regression, i.e., supervised learning with the experimental data as the learning data. A common multivariate analysis method is the so-called “genetic algorithm”, which is an evolutionary calculation method. This method efficiently approximates parameters to obtain optimal solutions by decreasing the possibility to terminate the optimization procedure at the local optimum by alternation of generations created by selection, crossover, and mutation operations [38, 39]. Ohenoja et al. applied a real-coded genetic algorithm to optimize seven parameters of an electrochemical model for polymer electrolyte membrane fuel cells, and tried to specify the range of each of those parameters [40]. Bozorgmehri et al. constructed an artificial neural network model whose objective function was the cell voltage for anode-supported SOFCs, and then optimized the maximum power density by using a genetic algorithm with four parameters, namely, anode support thickness, anode support porosity, electrolyte thickness and functional layer cathode thickness [41]. By applying such technologies into the multiple regression, the global optimal solution for a set of parameters can be obtained by iteration of the genetic algorithm.

In our work reported here, in order to develop a scheme to determine the surface coverage of the reactants at TPB on the electrode based on electrochemical measurement data, we applied the electrochemical reaction model developed by Ihara et al. [16] by considering the following three factors: (i) the coverage changes depending on the electrode potential (based on the assumption of local equilibrium between oxygen, oxide ion and electron in the electrolyte and on assumption of equilibrium between the oxide ion in the electrolyte and the oxygen adsorbent on the electrode surface); (ii) the model was constructed under the assumption of competitive adsorption, which is a common assumption in the thermochaly research field; and (iii) the model was composed of each elementally reaction step without approximations. This reaction model describes the Χ value that corresponds to the reaction rate as the competitive adsorption reaction of a chemical species, such as H, O, H2O and OH, and to the Langmuir reaction among these species. Then, in this work, the multiple regression, i.e., supervised learning with the experimental data as the learning data, was investigated with applying a genetic algorithm as an optimization method to determine the set of kinetics constant and equilibrium constants in our kinetics model. In order to determine the multiple variables by applying the reaction model and the algorithm of data fitting, we obtained a series of experimental data of both SOFC and SOEC reaction across the equilibrium potential under different gas conditions with H2/H2O/Ar mixture and a single cell with a commonly used cermet H2/H2O electrode of nickel (Ni)/yttria stabilized zirconia (YSZ) with well-defined structure. Finally, we developed the method to determine the surface property of SOFC/EC electrode, namely, the coverages of reactant at TPB by applying our kinetics model, the procedure to data optimization algorithm and the series of reversible SOFC/EC data. As a result, the experimental curves i vs. aO under 4 different P H2 × 3 different P H2O approximately fitted in SOFC region using one set of five independent variables. The coverage of chemical species at the TPB of Ni/YSZ during the SOFC power generation under wide range of the different oxygen activity was quantitatively determined.

2 Experimental

2.1 Cell Fabrication and Power Generation Experiments

Electrolyte-support type SOFC/EC cell was prepared using 8 mol.-% Y2O3-ZrO2 (8-YSZ; 20-mm diameter, 0.25-mm thick, TOSOH Co., Tokyo) as an electrolyte disc. For the H2/H2O electrode, a mixture paste of NiO (Kusaka Rare Metal Products, Co. Ltd., Tokyo) and 8-YSZ (TOSOH Co., Tokyo) was prepared at a weight ratio of 3:2 with adding ethylcellulose and α-terpineol at a weight ratio of 10:74. The paste was coated on the disc and was calcined on a 8-YSZ disc in air at 1,300°C for 4 h. Then, for the O2 electrode, a mixture paste of La0.8Sr0.2MnO3 (AGC Seimi Chemical Co. Ltd., Kanagawa) and ScSZ (Daiichi Kigenso Kagaku Kogyo Co., Ltd., Osaka) was coated on the other side of the disc and calcined on the other side of the 8-YSZ disc in air at 1,200°C for 4 h. Both H2/H2O electrode and O2 electrode were divided into working electrode (0.52 cm2) and reference electrode contacted to Pt mesh as the current collector. Both side electrodes with current collectors are attached to the end of inner tubes as the upper gas stream (10 mm in diameter). They were inserted into outer tubes as the downer gas stream (21 mm in diameter). The Pyrex glass ring, with the softening
point of 820 °C, was set between the end of outer tube on each side and the electrode disc pressed, and they were sealed by softening the glass rings with elevated temperature to 950 °C just before the SOFC/EC measurements. The performance of the sealing was confirmed by the open circuit voltage (OCV), which reached over 1.3 V under the dry H₂ supply to the H₂/H₂O electrode and O₂ to the O₂ electrode.

The operating temperature of the measurement was 900 °C. Pure O₂ was supplied to the O₂ electrode at a flow rate of 60 sccm. The H₂/H₂O electrode gas (mixture of H₂, H₂O and Ar) was supplied at partial pressures of H₂ (P₁H₂), H₂O (P₁H₂O) and Ar (P₁Ar) and at a total flow rate of 200 sccm, shown in Table 1. The measurement was carried out according to the order shown in Table 1. Before the measurement by applying current at each gas condition, the open circuit voltage was measured and confirmed to the equilibrium potential which can be calculated from the O₂ partial pressure in the H₂/H₂O electrode by assuming the thermal equilibrium of H₂/H₂O/O₂ in gas phase. In the measurement as reversible operation of SOFC/EC, the current density i applied with the interval of 50 mA cm⁻² from 0 to 1,000 mA cm⁻² and the interval of 100 mA cm⁻² from 1,000 to 1,900 mA cm⁻² in the FC region and the interval of at most 25 mA cm⁻² until the potential difference between H₂/H₂O and O₂ working electrode reached 1.5 V across OCV.

2.2 Measurement of i vs. Eₐ at different gas conditions

All the data with the number of total data points as 360 including the V at equilibrium with i = 0 in FC region and 177 in EC region among 12 conditions were obtained from the experiment at each i in different P₁H₂ and P₁H₂O, as described in 2.1 and as shown in Figure 2 using one cell. To minimize the effects of concentration overpotential and a shift in the Nernst potential in the measurement, the H₂ utilization at FC mode were kept lower than 7.8% and the water utilization at EC mode were kept lower than 24%, as shown in Table 1. As shown in Figure 2, the potential difference was measured between the (i) O₂ reference electrode (OR) and H₂/H₂O reference electrode (HR) (V₁OR–HR), (ii) O₂ working electrode (OW) and H₂/H₂O working electrode (HW) (V₁OW–HW), (iii) OR and OW (V₁OR–OW), (iv) HW and HR (V₁HW–HR), and (v) OR and HW (V₁OR–HW). The ohmic voltage loss of the HW and OW including ohmic voltage loss of the electrolyte, were identified using the current interruption method measured by an oscilloscope. The abrupt voltage change occurred in 5 μs and was defined as the ohmic voltage loss, and the ohmic voltage loss of HW and OW was defined as the difference between the voltage before the current interruption and the average voltage from 5 to 20 μs on V₁HW–HR and V₁OR–OW respectively. Then, the H₂/H₂O electrode overvoltage (ηₜₕ) was calculated as V₁HW–HR minus ohmic voltage loss. Here, the ohmic-free anode potential (Eₐ) defined as V₁OR–HW minus ohmic voltage loss of HW was confirmed by calculating the sum ηₜₕ + V₁OR–HR.

Also, in general, the reaction between H₂/O₂ and H₂O in the gas phase at the H₂/H₂O electrode in SOFC/EC, as shown in Eq. (1), reaches thermal equilibrium (equilibrium constant, $K = 10^{8.153}$ at 900 °C, thermodynamic data obtained from MALT, Materials-oriented Little Thermodynamic Database, Kagaku-Gijutsu Sha, Tokyo).

$$\text{H}_2 + \frac{1}{2}\text{O}_2 \leftrightarrow \text{H}_2\text{O} \quad (1)$$

Thus, the actual P₁H₂O during the electrochemical measurements at each i was also estimated based on the assumption of the equilibrium reaction Eq. (1) using $P_{O_2}$ which was calculated from V₁OR–HR ($P_{O_2} = 1$ at the O₂ electrode).

| Table 1 | H₂/H₂O electrode gas partial pressure used in this work. Maximum H₂ utilization at FC mode with $i = 1,900$ mA cm⁻², and maximum H₂O utilization at EC mode with $V = 1.5$ V. |
|-------|-----------------|-----------------|-----------------|-----------------|
| H₂/H₂O electrode gas (total 200 sccm) | H₂ utilization at FC | H₂O utilization at EC |
| $i = 1,900$ mA cm⁻² | $i = i$ (max) at $V = 1.5$ V |
| $P_{H_2}$ | $P_{H_2O}$ | $P_{Ar}$ | $i$ | $i$ |
| 1 | 0.99 | 0.01 | 0 | 2.7% | 24% |
| 2 | 0.97 | 0.03 | 0 | 2.6% | 17% |
| 3 | 0.95 | 0.05 | 0 | 2.5% | 16% |
| 4 | 0.80 | 0.01 | 0.19 | 3.4% | 20% |
| 5 | 0.80 | 0.03 | 0.17 | 3.3% | 15% |
| 6 | 0.80 | 0.05 | 0.15 | 3.0% | 15% |
| 7 | 0.50 | 0.01 | 0.49 | 4.7% | 17% |
| 8 | 0.50 | 0.03 | 0.47 | 4.8% | 15% |
| 9 | 0.50 | 0.05 | 0.45 | 5.0% | 15% |
| 10 | 0.30 | 0.01 | 0.69 | 7.8% | 16% |
| 11 | 0.30 | 0.03 | 0.67 | 7.6% | 16% |
| 12 | 0.30 | 0.05 | 0.65 | 7.0% | 15% |

Fig. 2. Configuration of four-electrode cell. Current flows between OW and HW (red line). $P_{H_2O}$ was calculated from $P_{O_2}$ determined by voltage difference between OR and HR (green line). $P_{O_2}$ at site 3 was calculated from ohmic-free voltage difference between OR [site 1] and HW [site 2] (blue line).
3 Results and Discussion

3.1 Derivation of Oxygen Activity $a_O$ at TPB from Ohmic-free Anode Potential vs. O$_2$ 1 atm ($E_a$)

Here, $a_O$ as shown in Eq. (2) was calculated from the ohmic-free anode potential via the following derivation process:

$$a_O = \exp \left(\frac{2FE_a}{RT}\right)$$  \hspace{1cm} (2)

where $E_a$ is expressed as $E_a = -(V_{HW-OW} + \Delta V_{ohmic} + \eta_o)$, $V_{HW-OW}$ is the potential difference between HW and OW, $\Delta V_{ohmic}$ is ohmic voltage loss of HW and OW, $\eta_o$ is O$_2$ electrode overvoltage between OW and OR, $F$ is Faraday constant, $R$ is gas constant, and $T$ is the temperature. The experimental cell was composed of four electrodes, as shown in Figure 1a and Figure 2: HW, HR, OW and OR on the electrolyte. The ohmic-free $E_a$ at TPB (site 3 in Figure 2) was determined by measuring the potential difference between OR (site 1) and HW (site 2) by the current interruption method. The $a_O$ was calculated from the electrochemical potential ($\Phi$) of the HW TPB as follows. The measured voltage difference between sites 1 and 2 ($E$), which corresponds to the difference in $\Phi$ of electrons ($\Phi_e$) between these two sites (Figure 2), is described in Eq. (3), where the number in parentheses is the site number.

$$-FE_a = \Phi_e(2) - \Phi_e(1) = (\Phi_e(2) - \Phi_e(3)) + (\Phi_e(3) - \Phi_e(1))$$  \hspace{1cm} (3)

When the following local equilibrium in oxide ion conductors such as YSZ or SrSZ, can be assumed as Eq. (4),

$$O + 2e^- = O^2-$$  \hspace{1cm} (4)

then $\Phi$ of $e^-$, O and O$^2-$ can be described, as shown in Eqs. (5) and (6).

$$\Phi_O + 2\Phi_e = \Phi_{O^2-}$$  \hspace{1cm} (5)

$$\Phi_e = 1/2(\Phi_{O^2-} - \Phi_O)$$  \hspace{1cm} (6)

Substituting $\Phi_e$ from Eq. (6) into Eq. (3) yields Eq. (7):

$$-FE_a = (\Phi_e(2) - \Phi_e(3)) + 1/2(\Phi_{O^2-}(3) - \Phi_O(1))$$

$$-1/2(\Phi_O(3) - \Phi_O(1))$$  \hspace{1cm} (7)

Here, ($\Phi_e(2) - \Phi_e(3)$) and ($\Phi_{O^2-}(3) - \Phi_O(1)$) are the ohmic voltage loss of the H$_2$/H$_2$O electrode and of the YSZ electrolyte, respectively. Then, by defining $E_a$ as ohmic-free voltage, Eq. (7) becomes Eq. (8).

$$FE_a = 1/2(\Phi_O(3) - \Phi_O(1))$$  \hspace{1cm} (8)

Because O is a neutral oxygen atom in the oxides and does not have any charge, its potential ($\Phi_O$) is described as Eq. (9).

$$\Phi_O = \Phi_{O^2-} + RT \ln a_O$$  \hspace{1cm} (9)

where $\Phi_{O^2-}$ is the standard electrochemical potential of O in the oxides. Thus, Eq. (8) becomes Eq. (10).

$$FE_a = 1/2(\Phi_{O^2-} + RT \ln a_O(3)) - 1/2(\Phi_{O^2-} + RT \ln a_O(1))$$

$$= 1/2RT \ln \frac{a_O(3)}{a_O(1)}$$  \hspace{1cm} (10)

When pure O$_2$ is supplied at the ideal state to the O$_2$ electrode, $a_O(1)$ can be considered as 1.

Here, we assumed a homogeneous $a_O$ in the oxide ion conductor of porous cermet H$_2$/H$_2$O electrode. Thus, $a_O(3)$, which corresponds to $a_O$ at TPB, is calculated as Eq. (11) and is also described as Eq. (2).

$$FE_a = 1/2RT \ln a_O(3)$$  \hspace{1cm} (11)

3.2 Relationship of $a_O$ and i on Different $P_{H_2}$ and $P_{H_2O}$

Figures 3a–3d show the I–V and I–P plots for the fuel cell for different gas mixtures at different $P_{H_2}$ and $P_{H_2O}$. The I–V is plotted both at the FC mode (positive i) and EC mode (negative i).
tive $i$, and $I-P$ is plotted at FC mode. In all 12 conditions, $i > 1.9 \text{ A cm}^{-2}$ were observed. The maximum power density was depending mainly on $P_{H2}$ and achieved 601 mW cm$^{-2}$ at $P_{H2} = 0.99$ and $P_{H2O} = 0.01$. The maximum power density changed slightly depending on $P_{H2O}$. Any obvious voltage drops at a high $i$ region caused by concentration overvoltage were not observed in any conditions. The open circuit potential ($i = 0$) depended on $P_{H2O}$ and quantitatively agreed with the calculated value by assuming thermal equilibrium of reaction Eq. (1). Figure 4 shows $i$ vs. $P_{H2O}$ at the EC region of $V_{OW-HW} = 1.3$ V and 1.4 V at different $P_{H2}$. In this region, $i$ was approximately linear to $P_{H2O}^{0.60-0.75}$ and slightly depended on $P_{H2}$. The maximum $i$ in the EC mode region was not high compared to that reported in the literature obtained at $P_{H2O} > 0.9$ A cm$^{-2}$ [42–44], because range of $P_{H2O}$ was 0.01–0.05 in this present study.

Figure 5 shows the relationship between log $a_O$ (calculated based on ohmic-free $E_a$) and log $|i|$ for different gas mixtures at different $P_{H2}$ and $P_{H2O}$. In these plots (Figure 5), the gradients of the slopes correspond to the nominal order of each reaction (guide $y = x$ are shown in each graph). The gradient of the slopes in the EC mode was around 1 and decreased with increasing $a_O$, and that in the FC mode was less than 1 and became more gradual at lower $a_O$. The $a_O$ vs. $i$ at each condition qualitatively agreed with previously reported data [16]. The curves at EC mode and the $a_O(eq)$ varied depending on both $P_{H2O}$ and $P_{H2}$, and the variation in $i$ vs. $a_O$ at the FC mode for the three different $P_{H2O}$ decreased at a high $a_O$ region ($> 10^{-8.5}$). The trend in the gradient was reflected by the coverage of each reactant at TPB. For example, the gradient of each slope at low $a_O$ in FC mode (i.e., near the equilibrium potential) was steeper than 1, due to partial cathodic current (= EC reaction), and then gradually decreased with increasing $a_O$. This tendency can be qualitatively explained by the increasing coverage of reactant at TPB with increasing $a_O$. Details and quantitative analysis of those slopes are described in the following sections.

### 3.3 Construction of Kinetics Model to Determine the Reactant Coverage at TPB

#### 3.3.1 Investigation of Models Based on Previous Literature

This work develops a scheme to determine the coverage of the reactants at TPB with a reaction model and a set of SOFC/EC measurement data. To select the reaction model, we investigated previously reported models with considering the existence of the following factors: (i) rate limiting reaction; (ii) assumptions in determining the relationship among the electrode potential, oxygen activity and oxygen coverage are the local equilibrium among oxygen, oxide ion and electron in the electrolyte and the equilibrium between the oxide ion in the electrolyte and the oxygen adsorbent on the surface; (iii) assumption in describing the relationship between the reaction rate and the coverage is competitive adsorption at TPB; and (iv) simplification or approximation of the relationship between the reaction rate and the coverage. The reaction models we investigated as candidates with these factors are shown in Table 2.
Mizusaki et al. proposed reaction kinetics based on local equilibrium of electrolyte and on equilibrium between the oxide ion and oxygen adsorbents on the electrode, as shown in Eqs. (12)–(14) [12].

$$O^{2-}(YSZ \text{ bulk}) \leftrightarrow O(YSZ \text{ bulk}) + 2e^- (YSZ \text{ bulk}) \quad (12)$$

$$2e^- (Ni) + O_{ad} \rightarrow O^{2-} (YSZ \text{ bulk}) + V_{ad} \quad (13)$$

$$e^- (Ni) \rightarrow e^- (YSZ \text{ bulk}) \quad (14)$$

Under these equilibrium conditions, the relationship between electrode potential and $\theta_O$ and that between $\theta_O$ and $\theta_v$ are uniquely determined. The reaction model has been discussed with the reaction order of $\theta_O$, $P_{H2}$, and $P_{O2}$ to $i$. Under the above assumptions, the rate limiting reaction was assumed to be the reaction between O$_{ad}$ at TPB and H$_2$. Wen et al. discussed the relationship between $P_{H2}/P_{H2O}$ and $i$ based on the relationship between anode overpotential and $\theta_O$ [13]. For both studies, $P_{H2}$ and $P_{H2O}$ were low, $\theta_O$ was assumed to be −1, and the competitive adsorption was not discussed [12,13].

On the other hand, the previous literatures including those two studies showed different relationships between $P_{H2}$ or $P_{H2O}$ and the electrode performance even though measurements were carried out with the common electrode material Ni/YSZ. Thus, Iwara et al. proposed a comprehensive SOFC/EC reaction model that can account for variation in DC polarization properties and AC impedance properties under different $P_{H2}$ and $P_{H2O}$ [16]. The model described the reaction as a Langmuir-type kinetics equation with competitive adsorption on TPB under local equilibrium in the electrolyte and under equilibrium between oxide ion and O$_{ad}$. That equation can be separated into two parts. One part is composed of the coverage ratio represented by adsorption equilibrium constants, which are independent of the geometric structure of the electrode and dependent only on the physical properties of Ni-YSZ. The other part is the kinetics constant, which depends on both the physical properties and geometric structure, such as porous structure or TPB length. The variation in reaction order of $\theta_O$, $P_{H2}$, and $P_{O2}$ to $i$ represents the values of the coverage ratio of chemical reactants vs. $\theta_O$, and thus $\theta$ at different conditions can be directly quantified.

Bieberle et al. established a scheme to simulate the reaction on a Ni/YSZ electrode based on six reversible reactions, as summarized in Section 1 (i.e., charge transfer $(O^{2-} + V_{ad,Ni} \rightarrow O_{ad,Ni} + V^0_{ad} + 2e^-)$, adsorption/desorption of H$_2$ and H$_2O$, and three surface chemical reaction including O$_2$ to H$_2O$, and the results suggested that the rate limiting step is the charge transfer reaction between the oxide ion and the surface oxygen adsorbents. In this model, the local equilibrium of oxygen in the electrolyte, oxide ion and electron was not assumed and the ratio of oxygen vacancy in the electrolyte was constant, independent of the anode potential, and thus the coverage of each reactant did not depend on the potential of the electrode. Also, the competitive adsorption to occupy the limited number of active sites was not investigated. Because the rate limiting step was suggested to be the charge transfer between the oxide ion and the surface oxygen, the coverage of each reactant was determined by the equilibrium of the reversible reaction in the model.

Zhu et al. proposed a reaction model with the sequential charge transfer pathway, as shown in Eqs. (15) and (16), assuming the rate limiting reaction, as Eq. (16) [19,20]

$$H(YSZ) + O^{2-} (YSZ) \equiv OH^- (YSZ) + e^- (Ni) + V(Ni) \quad (15)$$

| Factors in reaction model candidates to determine surface coverage of reactants of an electrode by data fitting. |
|---------------------------------------------------------------|
| **(a)** | **(b)** | **(c)** | **(d)** |
| Rate limiting reaction at TPB | Local equilibrium $O^{2-} \equiv O + 2e^-$ in the electrolyte | Equilibrium $O^{2-} (YSZ) + V_{ad}$ | Competitive adsorption at TPB | Simplification of the model |
| Mizusaki et al. [12] $H_2(g) + O_{ad} \rightarrow H_2O$ | O | O | $\theta_O - 1$ |
| Wen et al. [13] $OH_{ad} + H_2 \rightarrow H_2O_{ad}$ | O | O | $\theta_O - 1$ |
| Ibara et al. [16] $2H_{ad} + O_{ad} \rightarrow H_2O_{ad}$ | O | O | O |
| Bieberle et al. [17] $O_{ad} + V_{ad} \rightarrow O_{ad} + V_{O^{2-}} + 2e^-$ | – | O | – |
| Zhu et al. [19] $H (Ni) + OH^- (YSZ) \rightarrow H_2O (YSZ) + e^- (Ni) + V (Ni)$ | – | O | – |
| Bessler et al. [21] $H (Ni) + OH^- (YSZ) \rightarrow H_2O (YSZ) + e^- (Ni) + V (Ni)$ | – | O | – |
| Vogler et al. [22] $H (Ni) + O^{2-} (YSZ) \rightarrow OH (YSZ) + e^- (Ni) + V (Ni)$ | – | O | – | obtained rate constants from previous literature |
H(YSZ) + OH⁻(YSZ) ⇌ H₂O(YSZ) + e⁻(Ni) + V(Ni)  \hspace{1cm} (16)

The model was developed under the following equilibrium assumptions: (i) equilibrium of the dissociative adsorption, (ii) equilibrium of H₂O ads on Ni, (iii) adsorption equilibrium of H₂O(ad) on YSZ, (iv) equilibrium between the O²⁻ in YSZ bulk and the surface (by this equilibrium, the coverage of O²⁻ on YSZ is independent of the electrode potential), and (v) quasi-equilibrium of the electrochemical reaction, as shown in Eq. (15). By solving Eqs. (15) and (16) simultaneously with those equilibrium assumptions, the coverages \( \theta_{\text{H,YSZ}}, \theta_{\text{O},\text{YSZ},}, \theta_{\text{OH},\text{YSZ},}, \text{and } \theta_{\text{H},\text{YSZ},} \) were determined and the relationship between \( i \) and the ohmic-free anode potential \( \nu \) at the potential at the center of the electrolyte (\( E_i' \)) was described based on the Butler-Volmer type equation, as shown in Eq. (17):

\[
i = l_{\text{TPB}} \left[ \frac{k_a \theta_{\text{H,YSZ}} \theta_{\text{OH},\text{YSZ}}} {k_b \theta_{\text{O},\text{YSZ}}, \nu} \exp \left( \frac{\beta \nu} {RT} \right) \right]
\]

where \( l_{\text{TPB}} \) is the length of TPB, \( k_a \) and \( k_b \) are anodic and cathodic symmetric factors (\( k_a + k_b = 1 \)), and \( k_a \) and \( k_b \) are anodic and cathodic kinetics constants. In this model, whereas the local equilibrium of electrons and the equilibrium between O²⁻ in the electrolyte and O(ad) on the electrode were not assumed, the coverage of each species can be determined by fitting the model with two parameters, namely, the exchange \( i_{\text{ex}} \) and \( \beta \), to actual data. In this work, on the other hand, only the relationship between the overpotential and the coverage of OH⁻ was calculated by using the approximated equation under the assumption that \( \theta_{\text{O},\text{YSZ}} = 1 \) [19, 20].

Bessler et al. developed a reaction model of the SOFC/EC reaction [21] by generalizing the model developed by Bieberle et al. [17]. One reaction path or a series of two reaction paths was assumed and \( i \) was described as the difference between the rate of oxidation and reduction reactions, and each reaction rate was described by \( \nu \times \theta \times \theta \times \ldots \) where \( \times \) is the reaction order vs. \( \theta \). Then, the mass balance equations were described, based on all of the rate process including mass transfer, adsorption/desorption, reaction and/or charge transfer. The set of \( \theta \) values for steady state were numerically calculated, and the framework to simulate the relationship between \( i \) and the overpotential was proposed. By those methods, the multiple possible reaction pathways have been simultaneously investigated by Volger et al. [22] by substituting the following parameters of all of the processes without the charge transfer reaction, namely, the equilibrium constant of H₂, H₂O adsorption/desorption on Ni or YSZ [31–34], and the rate constant of the surface chemical reaction on Ni [31, 32] along with their temperature dependence from literature, the appropriate reaction path was suggested to be the reaction shown in Eqs. (15) and (16), and one of these two reactions was suggested as the rate determining step. In this method, because all of the rate constants are determined by fitting the rate of charge transfer reaction from reported data, the steady state coverage including the vacancy and the exponent of coverages corresponding to the kinetics order can be calculated. However, the accuracy of the values strongly depends on the equilibrium constants and rate constants obtained from literature. On the other hand, the electrode materials and/or the temperatures obtained from literature are not always the same as those in actual SOFC operations. For example, whereas most of the equilibrium constants and rate constants were obtained from the surface reaction and the adsorption/desorption equilibrium on Ni from calculated values of the heat of adsorption or the activation energy of the reaction on the metal surface including Ni (111) surface [45, 46], other constant values were obtained by using the extrapolated value from the temperature programmed desorption below 200°C [47], or using the experimental value for that on a rhodium (111) surface [45]. The constant value for the adsorption/desorption and the reaction on YSZ were obtained from the respective value at a temperature below 700°C at which the YSZ surface was mostly covered by OH [34]. Thus, quantifying the coverage at TPB by using the model [21, 22] involved using both a set of appropriate values of the rate and/or equilibrium constants obtained under conditions similar to an actual SOFC/EC reaction and a series of electrochemical measurement data under a wide range of conditions. Also, the model did not assume competitive adsorption, local equilibrium of oxygen, oxide ion and electron in the electrolyte, nor equilibrium of the oxide ion and the oxygen adsorbents, and thus the coverages of the reactants are determined independently by the electrode potential in the model.

Thus, this present work applies the electrochemical model to a H₂/H₂O electrode where the coverages of the reactants changes depending on the electrode potential assuming local equilibrium of oxygen, oxide ion and electron in the electrolyte and assuming equilibrium of the oxide ion and oxygen adsorbents [12, 13, 16]. Due to the competitive adsorption reaction, which is the general kinetics model in the thermochemical reaction, these assumptions are appropriate in the electrochemical model [16, 19]. Also, because the model by Ihara et al. [16] was developed with bottom-up with the elementary reactions without approximation of the equations, we decided to apply the model based on the model in ref. [16] into the scheme to determine the coverage of the reactants at TPB. The dependence of \( \theta_i / \theta_j \) on \( a_j \), \( P_{H_2} \) and \( P_{H_2O} \) becomes a component of the denominator in the Langmuir-type rate equation, and the value of \( \theta_i / \theta_j \) appears as the reaction order of \( i \) vs. \( a_j \). \( P_{H_2} \) and \( P_{H_2O} \). Conversely, based on the reaction order of \( i \) vs. \( a_j \), \( P_{H_2} \) and \( P_{H_2O} \) obtained in a wide range of experimental conditions, the value of \( \theta_i \) under such wide-ranging conditions can be determined. Thus, in this work, by applying the appropriate experimental data and using the method to optimize the multiple constants that are related to each other, the model can be used to determine the coverage \( \theta_i \), which is independent of the geometric structure of the electrodes. In addition, in the model in ref [16], whereas the rate limiting reaction was assumed to be the three-atom reaction of two...
H$_{\text{ad}}$ and O$_{\text{ad}}$ to generate H$_2$O$_{\text{ad}}$ on the surface, the probability of the three-atom reaction seems to be low [17], and numerous studies suggest the sequential reaction path including O$^2$-YSZ + H$_{\text{ad}}$ → OH$_{\text{YSZ}}$ [19–22], or O$_{\text{ad}}$ + H$_{\text{ad}}$ → OH$_{\text{ad}}$ [13]. Therefore, the surface chemical reaction in the model which we applied was modified as the consecutive reaction from O$_{\text{ad}}$ and H$_{\text{ad}}$ to OH$_{\text{ad}}$ and Had, which have been described as the simultaneous reaction of O$_{\text{ad}}$ and 2Had in [16].

3.3.2 Construction of the Model

Our kinetics model of the SOFC anode at TPB is composed of the Langmuir-type reaction model under competitive adsorption and equilibrium of charge transfer. The two candidates for the rate-determining reaction of the power generation, namely, reaction between H and O or between H and OH adsorbing on Ni near TPB can be represented, as in Eqs. (18) and (19).

\[ \text{H}_{\text{ad}} + \text{O}_{\text{ad}} \xrightarrow{k_1} \text{OH}_{\text{ad}} + \text{V}_{\text{ad}} \]  
(18)

\[ \text{H}_{\text{ad}} + \text{OH}_{\text{ad}} \xrightarrow{k_2} \text{H}_2\text{O}_{\text{ad}} + \text{V}_{\text{ad}} \]  
(19)

where \( k_1 \), \( k_2 \) and \( k_1 \), \( k_2 \) are rate constants of anodic and cathodic reactions, and \( V_{\text{ad}} \) is the density of vacant sites for adsorption at TPB. The total current density \( i \) is expressed with anodic and cathodic current \( (i_a \) and \( i_c \)), as shown in Eqs. (20) or (21).

\[ i = i_a - i_c = k_1 \theta_{\text{H}} \theta_{\text{O}} - k_2 \theta_{\text{OH}} \theta_{\text{V}} \]  
(20)

\[ i = i_a - i_c = k_2 \theta_{\text{H}} \theta_{\text{OH}} - k_1 \theta_{\text{H}_2\text{O}} \theta_{\text{V}} \]  
(21)

where \( \theta_{\text{H}} \), \( \theta_{\text{O}} \), \( \theta_{\text{H}_2\text{O}} \), and \( \theta_{\text{OH}} \), respectively, represent the coverage ratio of H$_{\text{ad}}$, O$_{\text{ad}}$, H$_2$O$_{\text{ad}}$, and OH$_{\text{ad}}$ on the absorption site. In both cases (Eqs. (18) and (19)), H$_2$O and H$_2$ are the respective competitive adsorption equilibrium states between the gas phase and Ni surface, as shown in Eqs. (22) and (23).

\[ \text{H}_2 + 2\text{V}_{\text{ad}} \xrightleftharpoons{k_{\text{H}}} 2\text{H}_{\text{ad}} \]  
(22)

\[ \text{H}_2\text{O} + \text{V}_{\text{ad}} \xrightarrow{k_{\text{H}_2\text{O}}} \text{H}_2\text{O}_{\text{ad}} \]  
(23)

where \( k_{\text{H}} \) and \( k_{\text{H}_2\text{O}} \) are the adsorption equilibrium constants for H$_2$ or H$_2$O, respectively. Also, the equilibrium between O in YSZ (O(YSZ)) and O$_{\text{ad}}$, Eq. (24),

\[ \text{O}(\text{YSZ}) + \text{V}_{\text{ad}} \xrightarrow{k_{\text{O}}} \text{O}_{\text{ad}} \]  
(24)

is assumed to be the combined equilibrium of reactions, as shown in Eqs. (25) to (27).

\[ \text{O}(\text{YSZ}) + 2e^- (\text{YSZ}) \xrightleftharpoons{k_{\text{O}}^e} O^2^- (\text{YSZ}) \]  
(25)

\[ O^2^- (\text{YSZ}) + V_{\text{ad}} \xrightarrow{k_{\text{O}_2\text{ad}}} \text{O}_{\text{ad}} + 2e^- (\text{Ni}) \]  
(26)

\[ e^- (\text{Ni}) \xrightarrow{k_{\text{e}}} e^- (\text{YSZ}) \]  
(27)

Combining Eqs. (25) to (27) yields \( K_{\text{O}} \), as shown in Eq. (28).

\[ K_{\text{O}} = K_{\text{O}_2}\cdot K_{\text{O}_2} K_{\text{e}}^2 \]  
(28)

Thus, \( \theta_{\text{H}} \), \( \theta_{\text{O}} \), and \( \theta_{\text{H}_2\text{O}} \) were obtained using the equilibrium assumptions, as shown in Eqs. (29) to (34).

\[ K_{\text{H}} = \frac{\theta_{\text{H}}^2}{i_{\text{H}_2} \cdot \theta_{\text{V}}} \]  
(29)

\[ \theta_{\text{H}} = \sqrt{K_{\text{H}} P_{\text{H}_2} \cdot \theta_{\text{V}}} \]  
(30)

\[ K_{\text{H}_2\text{O}} = \frac{\theta_{\text{H}_2\text{O}}}{P_{\text{H}_2\text{O}} \theta_{\text{V}}} \]  
(31)

\[ \theta_{\text{H}_2\text{O}} = K_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}} \cdot \theta_{\text{V}} \]  
(32)

\[ K_{\text{O}} = \frac{\theta_{\text{O}}}{i_{\text{c}} \theta_{\text{V}}} \]  
(33)

\[ \theta_{\text{O}} = K_{\text{O}} \theta_{\text{O}} \cdot \theta_{\text{V}} \]  
(34)

Here, \( \theta_{\text{OH}} \) depends on which reaction (Eq. (18) or (19)) is the rate-determining reaction. We assumed one of them as a quasi-equilibrium due to their fast reaction rate, while the other one as the rate-determining reaction:

Case 1: \( \text{H}_{\text{ad}} + \text{O}_{\text{ad}} \leftrightarrow \text{OH}_{\text{ad}} + \text{V}_{\text{ad}} \) as the rate determining reaction

When reaction Eq. (18) is the rate-determining reaction, reaction Eq. (19) reaches quasi-equilibrium, as shown in Eq. (35).

\[ \text{H}_{\text{ad}} + \text{OH}_{\text{ad}} \xrightarrow{k_{\text{H}_2\text{O}}} \text{H}_2\text{O}_{\text{ad}} + \text{V}_{\text{ad}} \]  
(35)

Under this equilibrium case Eq. (36) is

\[ K_{\text{OH}_2} = \frac{\theta_{\text{OH}_2} \theta_{\text{V}}}{i_{\text{H}_2} \theta_{\text{OH}} \theta_{\text{V}}} \]  
(36)

Thus, \( \theta_{\text{OH}} \) and \( \theta_{\text{V}} \) are obtained using Eqs. (30) and (32) as Eqs. (37) and (38).
\[
\theta_{OH} = \frac{\theta_H P_{H2}}{K_{OH2} \theta_H} = \frac{K_{H2O} P_{H2}}{K_{OH2} \sqrt{K_H} P_{H2}} \theta_V 
\]

(37)

\[
\theta_V = 1 - \theta_O - \theta_H - \theta_{H2O} - \theta_{OH} 
= \frac{1}{1 + K_{OH2} \theta_H + K_{H2O} P_{H2O} + \frac{K_{H2O} P_{H2O}}{K_{OH2} \sqrt{K_H} \theta_H}} 
\]

(38)

Finally, by substituting Eqs. (30), (32), (34), (37), and (38) into Eq. (20), \(i\) can be described as in Eq. (39) with \(i_a\) and \(i_c\) as partial anodic and cathodic current density, respectively.

\[
i = i_a - i_c = \frac{k_a \sqrt{K_H} P_{H2} K_{OH2}}{(1 + K_{OH2} \theta_H + K_{H2O} P_{H2O} + \frac{K_{H2O} P_{H2O}}{K_{OH2} \sqrt{K_H} \theta_H})^2} 
\]

(39)

Based on Eq. (39), the range of the nominal reaction order of \(a_O, p_{H2},\) and \(P_{H2O}\) to \(i\) can be represented as follows, depending on the variation in magnitude between the terms in the dominator of Eq. (39).

Under a fully polarized anodic condition, \(i\) can be assumed to be \(i_a\) if \(\theta_{OH}/\theta_V\) is relatively lower than 1, which means \(\theta_{OH}\) is much lower than \(\theta_V\) and thus \(i\) of the power generation based on Eq. (39) can be approximated as

\[
i \approx i_a \simeq \frac{k_a \sqrt{K_H} P_{H2} K_{OH2}}{(1 + K_{OH2} \theta_H + K_{H2O} P_{H2O})^2} \]  

(40)

The range of the nominal reaction orders of \(a_O, p_{H2},\) and \(P_{H2O}\) to \(i\) can be considered as follows. For example, if \(\theta_{OH}/\theta_V = K_{OH2} \theta_H\) is relatively much larger than \(1 + \sqrt{K_H} P_{H2} + K_{H2O} P_{H2O}\), Eq. (40) becomes

\[
i \approx i_a \simeq \frac{k_a \sqrt{K_H} P_{H2} K_{OH2}}{(K_{OH2} \theta_H)^2} \]  

(41)

and if \(\theta_{OH}/\theta_V\) is much smaller than 1, Eq. (40) becomes

\[
i \approx i_a \simeq \frac{k_a \sqrt{K_H} P_{H2} K_{OH2}}{(1 + \sqrt{K_H} P_{H2} + K_{H2O} P_{H2O})^2} \]  

(42)

Finally, the range of the nominal reaction orders of \(a_O, p_{H2},\) and \(P_{H2O}\) to \(i_a\) are included in Eq. (43).

\[-1 \leq \frac{d \log_2 i}{d \log_2 i_a} \leq 1, \quad -1.5 \leq \frac{d \log_1 i}{d \log_1 i_a} \leq 0.5, \quad -2 \leq \frac{d \log_2 i}{d \log_2 i_a} \leq 0 \]  

(43)

On the other hand, if \(\theta_{OH}/\theta_V\) is relatively much higher than \(1 + K_{OH2} \theta_H + K_{H2O} P_{H2O}\). Eq. (39) can be approximated as Eq. (44) and the nominal reaction order can be represented as following Eq. (45).

\[
i \simeq i_a \simeq \frac{k_a \sqrt{K_H} P_{H2} K_{OH2}}{(K_{OH2} \theta_H)^2} \]  

(44)

\[
\frac{d \log_2 i}{d \log_2 i_a} = 1, \quad \frac{d \log_1 i}{d \log_1 i_a} = 1.5, \quad \frac{d \log_2 i}{d \log_2 i_a} = -2 \]  

(45)

Case 2: \(OH_{ad} + H_{ad} \leftrightarrow H_2O_{ad} + V_{ad}\) as the rate-determining reaction

When reaction Eq. (19) is the rate-determining reaction, reaction Eq. (18) reaches quasi-equilibrium, as shown in Eq. (46).

\[H_{ad} + O_{ad} \leftrightarrow OH_{ad} + V_{ad} \]  

(46)

Under this equilibrium as Eq. (47).

\[
K_{OH1} = \frac{\theta_{OH} \theta_V}{\theta_H \theta_O} \]  

(47)

Thus, \(\theta_{OH}\) and \(\theta_V\) are obtained using Eqs. (30) and (34), as shown in Eqs. (48) and (49).

\[
\theta_{OH} = \frac{K_{OH1} \theta_H}{\theta_V} = \frac{K_{OH1} \theta_H}{K_{OH2} \theta_H} \]  

(48)

\[
\theta_V = \frac{1}{1 + K_{OH2} \theta_H + \sqrt{K_H} P_{H2} + K_{H2O} P_{H2O} + K_{OH1} K_{OH2} \theta_H \theta_V} \]  

(49)

Finally, by substituting Eqs. (30), (32), (34), (48), and (49) into Eq. (21), \(i\) is described, as shown in Eq. (50).

\[
i = \frac{k_2 K_H P_{H2} K_{OH1} K_{OH2}}{(1 + K_{OH2} \theta_H + \sqrt{K_H} P_{H2} + K_{H2O} P_{H2O} + K_{OH1} K_{OH2} \theta_H)^2} 
\]  

(50)

Under a fully polarized anodic condition, \(i\) can be assumed to be \(i_a\) if \(\theta_{OH}/\theta_V\) is relatively lower than 1, which means \(\theta_{OH}\) is much lower than \(\theta_V\) and thus \(i\) of the power generation based on Eq. (50) can be approximated as Eq. (51).

\[
i \simeq i_a \simeq \frac{k_2 K_H P_{H2} K_{OH1} K_{OH2}}{(1 + K_{OH2} \theta_H + \sqrt{K_H} P_{H2} + K_{H2O} P_{H2O})^2} \]  

(51)
The range of the nominal reaction orders of \( a_O, P_{H2}, P_{H2O} \) to \( i \) can be considered as follows. For example, if \( \theta_O/\theta_V = K_{pO} \) to \( i \) is significantly larger than 1 + \( \sqrt{K_{pH2}K_{OHH}K_{pO}} \), then Eq. (51) becomes

\[
i \approx i_r \approx \frac{k_2K_{pH2}K_{OHH}K_{pO}}{(K_{pO})^2} = \frac{k_2K_{pH2}K_{OHH}K_{pO}}{K_{pO}} \tag{52}
\]

and if \( \theta_O/\theta_V \) is smaller than 1, Eq. (51) becomes

\[
i \approx i_r \approx \frac{k_2K_{pH2}K_{OHH}K_{pO}}{(1 + \sqrt{K_{pH2}K_{OHH}K_{pO}})^2} \tag{53}
\]

On the other hand, if \( \theta_{OH}/\theta_V \) is relatively larger than 1 + \( K_{OH} + \sqrt{K_{pH2}K_{OHH}} + K_{pH2O} \), then Eq. (50) can be approximated as Eq. (54) and the nominal reaction order can be represented as follows.

\[
i \approx i_r \approx \frac{k_2K_{pH2}K_{OHH}K_{pO}}{(K_{OHH}K_{pO})} = \frac{k_2}{K_{pH2}K_{OHH}K_{pO}} \tag{54}
\]

Finally, the range of the nominal reaction orders of \( a_O, P_{H2}, P_{H2O} \) to \( i \) are included in the range as follows:

\[
-1 \leq \frac{d \log i}{d \log a_O} \leq 1, \quad 0 \leq \frac{d \log i}{d \log P_{H2}} \leq 1, \quad -2 \leq \frac{d \log i}{d \log P_{H2O}} \leq 0 \tag{55}
\]

Thus, the rate determining reaction at TPB can be assumed to be the nominal reaction orders of \( a_O, P_{H2}, P_{H2O} \) to \( i \) at the fully polarized anodic region as \( i = i_r \). As shown in Figure 5 (a–d), regardless of \( P_{H2} \) and \( P_{H2O} \), the reaction order of \( a_O \) to \( i_r \) was around 1, which allows both Cases 1 and 2. As for \( P_{H2} \) and \( P_{H2O} \), Figure 6 shows \( i \) vs. \( P_{H2O} \) (a–d) and \( i \) vs. \( P_{H2} \) (e–h) with a double logarithm axis under the fully polarized anodic region, \(-8.3 < \log a_O < -8.0\), with line guides \( y = x \) (a–d) and \( y = x \) (e–h). The gradient of the plots corresponds to the reaction order of \( P_{H2O} \) (a–d) or \( P_{H2} \) (e–h) to \( i_r \). The reaction order of \( P_{H2O} \) to \( i_r \) was –0.33 – 0 and depended on \( a_O \) and \( P_{H2} \). It was higher at larger \( a_O \) and/or at smaller \( P_{H2} \). That of \( P_{H2} \) to \( i_r \) was around 1 regardless of \( a_O \) and \( P_{H2O} \). In Case 1, the reaction order of \( P_{H2} \) to \( i_r \) was –1.5 – 0.5 at low \( \theta_{OH}/\theta_V \) or 1.5 at high \( \theta_{OH}/\theta_V \) and thus Case 1 cannot describe the experimental data, where the reaction order of \( P_{H2} \) to \( i_r \) is around 1 regardless of \( a_O \) and \( P_{H2O} \). In Case 2, on the other hand, the reaction order of \( P_{H2O} \) to \( i_r \) was 1 when \( \theta_{OH}/\theta_V \) and \( \theta_{OH}/\theta_V \) were relatively low, and thus Case 2 can describe the experimental data with the appropriate set of \( K_{pH2}, K_{OH}, K_{pH2O} \) and \( K_{OHH} \). Thus, Case 2 with the kinetics Eq. (50) is valid for SOFC reaction. Although the rate determining step of the anode reaction has been extensively discussed, the process of hydrogen oxidation reaction is a common step. For example, Wen et al. assumed the rate of \( H_{H2ad} \) generation from \( H_{ad} \) and \( OH_{ad} \) is the key to decrease the anode overpotential [13], and Zhu et al. assumed the rate determining step as the reaction of \( H_{Ni} + OH_{YSZ} \) [19, 20]. In the following discussion, for convenience, \( k_2, k_2, k_2, \) and, respectively, \( K_{pH2}, K_{OHH} \) in Eq. (50) are denoted as \( k_x, k_x, k_x, \) and \( K_x, K_x, K_x, \) respectively.

Thus, the reaction model of the present work is described as Eq. (50). This equation is composed of six constants with four equilibrium constants (\( K_{OH}, K_{H2}, K_{H2O}, \) and \( K_{OH} \)) and two kinetics constants (\( k_x, k_x \)) under four experimental parameters (\( i, P_{H2}, P_{H2O}, \) and \( a_O \)). The effect of the coverage ratio \( \theta_x/\theta_y (x = O, H, H_2O \) and \( OH \) described with the set of \( k_x, k_x, k_x, \) and \( K_x, K_x, K_x, \) respectively.

---

Fig. 6 (a–d) \( i \) vs. \( P_{H2O} \) and (e–h) \( i \) vs. \( P_{H2} \) with the double logarithm axis at different (a–d) \( P_{H2} \) and (e–h) \( P_{H2O} \) under FC region with \( \log a_O = -8.0 \) (a, e), –8.1 (b, f), –8.2 (c, g), and –8.3 (d, h).
\( P_{1H2}, P_{1H2O}, \) and \( a_O \) as shown in then denominator in Eq. (50), then the values of \( \theta_i/\theta_V \) reflects the reaction order of \( x \) to \( i \). Thus, by preparing a sufficient number and wide range of experimental data of \( i \) vs. \( a_O \) at both SOFC region with higher \( a_O \) than \( a_O \) at equilibrium (\( a_O(eq) \)) and EC regions with lower \( a_O \) than \( a_O(eq) \) under different \( P_{1H2} \) and \( P_{1H2O} \), the values of \( \theta_i/\theta_V \) under the different \( a_O, P_{1H2}, \) and \( P_{1H2O} \) can be determined. Also, because the relationship between \( i \) and each \( k_c \) is not independent from each other, particularly, \( \theta_{OH}/\theta_V \) is described with the combination of multiple variables as \( K_{OH}, K_{OH}K_{OH}(K_{H2}P_{1H2})^{1/2} \), an appropriate method to optimize the multiple parameters is required. By optimizing the values of equilibrium constant by those experimental data and optimization algorithm, Eqs. (29), (31), (33), and (47), \( \theta_{H2}, \theta_{H2O}, \theta_{OH}, \) and \( \theta_{OH} \) on the active site of TPB can be determined.

3.4 Determination of Model Parameters by Using Genetic Algorithm with SOFC/EC Data

3.4.1 Balance of Kinetics Constant Between FC and EC

First, \( a_O(eq) \) in which there is no current in either the EC or FC direction, can be set in the model as shown in Eq. (56):

\[
i = 0 \quad \text{at} \quad a_O = a_O(eq) \quad (56)
\]

In this case, according to Eq. (50), it becomes as shown in Eq. (57).

\[
k_sK_{H2}P_{H2}K_{OH}K_{OH}a_O(eq) - k_pK_{H2O}P_{H2O} = 0 \quad (57)
\]

Then, \( k_i/k_s \) is described in terms of other variables and \( k_c \) becomes a dependent variable as Eq. (58):

\[
k_c = \frac{P_{H2}a_O(eq)}{P_{H2O}} \frac{K_{H2}K_{OH}K_{OH}K_{OH}}{P_{H2O}} \quad (58)
\]

\( P_{H2}P_{O2}^{1/2}/P_{H2O} \) is a constant value of \( 10^{-8.153} \) at 900°C, because the \( H_2/O_2 \) electrode reaches the thermal equilibrium of reaction Eq. (1), and the \( P_{O2} \) at the \( H_2/O_2 \) electrode is \( \exp(4FE_{eq}/RT) \) when \( P_{O2} \) at the \( O_2 \) electrode is 1. Thus, \( P_{H2O(eq)}/P_{H2O} \) also becomes constant at \( 7 \times 10^{-9} \) for any \( P_{H2}/P_{H2O} \), and finally \( k_i/k_s \) can be described as a constant value, and \( K_{H2}, K_{OH}, K_{OH}, \) and \( k_c \) become dependent variables in Eq. (50).

As a result, \( i \) can be described based on Eq. (50) as Eq. (59) by using \( a_O(eq) \), which can be calculated by the equilibrium of \( H_2/O_2/O_2 \) under \( P_{H2} \) and \( P_{H2O} \), and be confirmed experimentally by OCV.

\[
i = \frac{k_pK_{H2}P_{H2}K_{OH}K_{OH}(a_O - a_O(eq))}{(1 + K_{OH}a_O + \sqrt{K_{H2}P_{H2} + K_{H2O}P_{H2O} + K_{OH}K_{OH}a_OK_{OH}P_{H2O})^{2}} \quad (59)
\]

Thus, the remaining independent variables are \( k_p, K_{H2}, K_{OH}, \) and \( K_{H2O} \). 3.4.2 Genetic Algorithm to Determine the Kinetics Constant and Equilibrium Constants

The next step is to determine the kinetics constant \( k_p \) and the equilibrium constants \( K_{H2}, K_{OH}, K_{H2O}, \) and \( K_{OH} \) by data fitting of the power generation data for SOFC/EC. The supervised machine learning approach with the experimental data as the learning data and the genetic algorithm as an optimization method was developed. The real-coded genetic algorithm was applied to determine the optimal values of these five parameters of the model equation Eq. (59) for the power generation data. Figure 7 shows the flowchart of the analysis method using the genetic algorithm. It is a repetitive process of the following overall steps: (i) generate the first population of multiple individuals which are candidates for the parameter set (individual is defined here as the set of five parameters) [38, 39]; (ii) generate the next population composed of the same number of individuals as the first population by using three operations, namely, selection, crossover, and mutation [38, 39]; (iii) evaluate each new individual based on a quantitative index, such as the mean squared error (MSE). First, we prepared 200 individuals, where each had a set of five random numbers with the ranges of \(-500 < \log k_p \leq 500 \) as the process of (1) in Figure 7. To generate a new population, the tournament selection method, which is a common selection method, was applied to obtain 30 individuals [39] by selecting two candidates randomly from the previous generation and then choosing the individual with the lower MSE, as shown in Figures 7 (2) and 7 (3). In the two-point crossover method used here, one of the parameters (except \( K_{H2O} \) as explained in the next paragraph) is exchanged between the randomly selected 2 individuals from the 30 individuals selected by the tournament selection method [39]. Thus, 30 new individuals were created by conducting such crossover for each of the four other parameters, thus generating a total of 120 individuals, as shown in Figure 7 (4). In the mutation method, after picking one individual selected by the tournament selection method, one of the five parameters in that individual was randomly changed. In our work, 10 individuals were randomly picked to apply mutation for each of the five parameters, thus generating a total of 50 individuals, as shown in Figure 7 (5). Next, a new generation population of 200 individuals was created (whose name was the same as that in the previous generation population) by merging the 30 new individuals from the selection, the 120 from crossover, and the 50 from mutation, as shown in Figure 7 (6).

In the genetic algorithm, the balance between the calculation cost, i.e., computational complexity, and the probability to achieve the global optimal solution can be controlled by adjusting the number of individuals in the crossover and mutation operations in generating the next-generation candidates from the previous generation [39]. In preliminary analysis operation, we initially used 500 individuals per population,
including the crossover of every parameter including \(K_{H_2O}\), and performed 100 iterations of the entire process. As a result, \(K_{H_2O}\) was determined as an unique value in the early iterations, and thus crossover operation on \(K_{H_2O}\) did not work efficiently. Consequently, to reduce the calculation time in the formal analysis operation, the number of individuals was reduced to 200, and only mutation was applied to \(K_{H_2O}\). The process was repeated by creating a new generation \(vi\) and performed 100 iterations of the entire process. As a result, \(80\) was set as the final number of generations because the values converged in about 80 iterations, as shown in Figure 7 (7).

The solution obtained by the genetic algorithm was used as the initial solution, and the optimal solution was converged by using the gradient descent method, as shown in Figure 7 (8). Considering the possibility that the obtained optimal solution is a local optimal solution, the global optimal solution was searched by repeating the following process more than 50,000 times using the simulation tool MATLAB/SIMULINK, as shown in Figure 7 (9). The MSE was used as an index for determining the goodness of fit, and is the error function expressed as in Eq. (60)

\[
MSE = \frac{1}{N} \sum_{i=1}^{N} \left( \log i_{\text{exp}} - \log i_{\text{calc}} \right)^2
\]

where \(i_{\text{exp}}\) is the experimental value of \(i\), and \(i_{\text{calc}}\) is the value calculated by using our kinetics model Eq. (60) (in this work, \(N = 348\) is the total number of data points of SOFC operation under 12 conditions).

As a result, the optimal solution with the smallest MSE (0.06345) was observed as the global optimal solution among the obtained optimal solutions. In this analysis, 2,272 sets of optimal solution combinations were detected in more than 50,000 optimal solutions. Figure 8 shows the 2,272 sets of optimal solution candidates of \(K_{OH}\) (a), \(K_{H}\) (b), \(K_{O}\) (c), \(K_{H2O}\) (d), and \(k_o\) (e) obtained by the fitting method using the genetic algorithm. The horizontal axis shows the data number when \(K_{OH}\) is arranged in ascending order, and the vertical axis shows the exponent of each parameter. Here, \(log K_{H2O}\) was 0.5044 for all the parameter sets. In contrast, as \(K_{OH}\) increased, the range of \(k_o\), \(K_{H2O}\), and \(K_{O}\) broadened. Nine representative examples of these optimal solution candidates are plotted as different colored circles in Figure 8, and summarized in Table 3. No. 1 and No. 2 are combinations with maximum and minimum \(K_H\) in the candidate group obtained in this analysis, and No. 3 and No. 4 are combinations with maximum and minimum \(K_O\). In all the 2,272 parameter sets, \(K_{OH}K_{O}K_{H^{1/2}}\) and \(K_{K^{1/2}}\) showed constant values. Because \(\theta_{K^{1/2}}\) under the constant \(a_{OH}\) and \(P_{H2}\) became constant, so \(K_{OH}K_{H^{1/2}}\) also was determined to be a constant value. Then, the numerator of Eq. (59), which can be expressed as \(k_oK^{1/2}\times K_{OH}K_{O}K^{1/2}\times P_{H2}(\theta_{O}a_{O(eq)})\), was also constant and both \(K_{OH}K_{H^{1/2}}\) and \(P_{H2}(\theta_{O}a_{O(eq)})\) were already determined, so \(k_oK^{1/2}\) under the constant \(i_{pH}\) and \(a_{O(eq)}\) was also determined uniquely. Thus, \(K_{OH}K_{H^{1/2}}\) and \(k_oK^{1/2}\) were determined by fitting the experimental data, and \(\theta_{K^{1/2}}\) which was composed of \(K_{OH}K_{H^{1/2}}, a_{OH}\), and \(P_{H2}\) was determined. Then, the numerator of Eq. (59), which was composed of \(k_oK^{1/2}, K^{1/2}, P_{H2}(\theta_{O}a_{O(eq)})\), was also determined.
A sensitivity analysis was carried out for $K_{OH}$, $K_{H}$, $K_{H2O}$, and $K_{OH}$ to confirm that the obtained solutions are globally optimal solutions. Each reaction and equilibrium constant was fixed, and optimization was performed using the other four parameters. Figure 9 shows the sensitivity analysis results. $K_{H2O}$ has the unique value that MSE was minimum when log $K_{H2O}$ was 0.5044 as shown in Figure 9b. The minimum MSE was observed when log $K_{H} < -9$ (Figure 9a), log $K_{O} < 5$ (Figure 9c), and log $K_{OH} > 8$ (Figure 9d). The values of the parameters in Table 3 and Figure 8 are in this range. In the Supporting Information, figure S1 shows additional sets of $K_{x}$ values, focusing on $K_{H}$ (red circles), $K_{O}$ (black), and $K_{OH}$ (green). For example, the red circles in Figures S1b–S1d show the values of log $K_{H2O}$, log $K_{O}$, and log $K_{OH}$ when optimized by fixing log $K_{H} = -100$ (Figure S1a). The circles and triangles show the parameter values when the MSE was the minimum and the squares show when the MSE was the local optimal solution. The circles and triangles were in the range of log $K_{H} < -9$, log $K_{O} < 5$, and log $K_{OH} > 8$ for all parameters, and log $K_{H2O}$ converged at 0.5044. In contrast, the squares reveal that none of the parameters reached the global optimal solution. Therefore, the solution obtained in our analysis is a global optimum solution. When log $K_{O} > 12$, log $K_{H} > 8$, and log $K_{OH} < 2$, MSE had a constant value and the parameters had converged on local minimum.

### 3.5 Evaluation of Coverage at TPB by the Kinetics Model

Based on the results shown in Section 3.3, the relationship between the coverage of each adsorbent on the active site of TPB ($\theta_{H}$, $\theta_{O}$, $\theta_{H2O}$, $\theta_{OH}$ and $\theta_{V}$) and $k_a$ at different $P_{H2}$ and $P_{H2O}$ were evaluated, as shown in Figures 10a–10c. The coverage curves were fitted by using the parameter set of the nine representative examples of the optimal solution candidate in Table 3 and superimposed on each plot (Figures 10a–10c). When all the parameter sets in Figure 8 were superimposed on each plot, the curves for $\theta_{H2O}$, $\theta_{OH}$, and $\theta_{V}$ were all the same in every conditions. In contrast, $\theta_{H}$ and $\theta_{O}$ show different curves depending on the multiple optimized parameter set, but had negligibly small values even in high $a_O$ and $P_{H2}$.

### Table 3 Parameter sets of representative examples of these optimal solution groups in Figure 8.

| No. | $k_a$ / $10^9$ | $K_{H}$ / $10^9$ | $K_{OH}$ / $10^9$ | $K_{O}$ / $10^9$ | $K_{H2O}$ / $10^9$ | $K_{OH} \sqrt{K_{H}}$ / $10^9$ | $k_a \sqrt{K_{H}}$ / $10^9$ | MSE |
|-----|----------------|-----------------|------------------|-----------------|-----------------|----------------------|----------------------|-----|
| No. 1 | 7.401 | -12.62 | 11.60 | 2.224 | 0.5044 | 7.059 | 1.089 | 0.06345 |
| No. 2 | 65.34 | -128.5 | 308.2 | -236.5 | 0.5044 | 7.059 | 1.089 | 0.06345 |
| No. 3 | 161.1 | -320.0 | 162.7 | 4.819 | 0.5044 | 7.059 | 1.089 | 0.06345 |
| No. 4 | 9.080 | -15.98 | 303.6 | -288.1 | 0.5044 | 7.059 | 1.089 | 0.06345 |
| No. 5 | 83.18 | -164.2 | 240.6 | -151.0 | 0.5044 | 7.059 | 1.089 | 0.06345 |
| No. 6 | 148.8 | -295.5 | 240.6 | -85.38 | 0.5044 | 7.059 | 1.089 | 0.06345 |
| No. 7 | 7.592 | -13.00 | 105.5 | -91.45 | 0.5044 | 7.059 | 1.089 | 0.06345 |
| No. 8 | 7.277 | -12.38 | 198.7 | -185.0 | 0.5044 | 7.059 | 1.089 | 0.06345 |
| No. 9 | 7.257 | -12.34 | 164.1 | -150.4 | 0.5044 | 7.059 | 1.089 | 0.06345 |
All of the 2,272 parameter sets show the same result, namely, $\theta_{\text{H}_2\text{O}}$, $\theta_{\text{OH}}$, and $\theta_{\text{H}}$ had the same curves, and $\theta_1$ and $\theta_0$ had small values. Therefore, the coverages were uniquely determined for any combination despite the existence of many optimal parameters. Finally, by applying Eq. (61), $i$ can be approximated as follows:

$$i = \frac{k_a K_H^{1/2} \times K_{\text{OH}} K_{\text{H}_2\text{O}} K_H^{1/2} \times P_{\text{H}_2} (a_0 - a_{0(\text{eq})})}{\left(1 + K_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}} + K_{\text{OH}} K_{\text{H}_2\text{O}} K_H^{1/2} \times a_0 P_{\text{H}_2}^{1/2}\right)^2}$$

The constant values of $K_{\text{H}_2\text{O}} = 3.194$, $K_{\text{OH}} K_{\text{H}}^{1/2} = 1.146 \times 10^7$, and $k_a K_H^{1/2} = 12.27$ were determined by our experimental data in this work. In the range of $10^{-6} < a_0 < 10^{-2}$, the range of each coverage was $0.94 < \theta_{\text{H}_2\text{O}} > 0.35$, $0.15 > \theta_{\text{OH}} > 0.049$, $0.022 < \theta_{\text{H}} < 0.57$, $\theta_1 < 10^{-6}$ and $\theta_0 < 10^{-4}$. The coverage $\theta_{\text{OH}}$ depended on $a_0$ and $P_{\text{H}_2}$ but not on $P_{\text{H}_2\text{O}}$ and was negligibly small at $a_0 < 10^{-5}$ and relatively high at $a_0 > 10^{-4}$. The coverage $\theta_{\text{H}_2\text{O}}$ depended on both the feedstock $P_{\text{H}_2\text{O}}$ condition and $a_0$. It increased with increasing $a_0$ because $\text{H}_2\text{O}$ is the reaction product of fuel cells, and $P_{\text{H}_2\text{O}}$ increases with increasing $i$ and then $\theta_{\text{H}_2\text{O}}$ decreases with further increasing $a_0$ due to the increase in $\theta_{\text{OH}}$ and the decrease in $\theta_{\text{H}}$. Figure S2 (a–c) shows the relationship between $i$ and $\theta_{\text{H}_2\text{O}}$, and Figure S3 (a–c) shows the relationship between $i$ and $\theta_{\text{OH}}$ (see Supporting Information). Whereas $\theta_{\text{OH}}$ and $\theta_{\text{H}_2\text{O}}$ depended on $i$, both $P_{\text{H}_2}$ and $P_{\text{H}_2\text{O}}$ and their variation correspond to the variation in $\theta_{\text{H}_2\text{O}}$ and $\theta_{\text{H}_2\text{O}}/\theta_{\text{H}}$ was independent of $P_{\text{H}_2\text{O}}$ and linearly increased with increasing $i$. This trend suggests that $\theta_{\text{H}_2\text{O}}/\theta_{\text{H}}$ simply depends on $P_{\text{H}_2\text{O}}$ at the $\text{H}_2/\text{H}_2\text{O}$ electrode, where $\text{H}_2\text{O}$ comes both from the feedstock and from the power generation reaction. Both $\theta_{\text{H}}$ and $\theta_{\text{H}_2\text{O}}$ were negligibly small, regardless of $a_0$, $P_{\text{H}_2}$, and $P_{\text{H}_2\text{O}}$. Thus, in FC mode, $\theta_{\text{H}_2\text{O}}$ is governed mainly by $\theta_{\text{OH}}$ and $\theta_{\text{H}_2\text{O}}$. In our previous study [16], the nominal reaction order against $P_{\text{H}_2}$ at higher $P_{\text{H}_2}$ was less than 1, which seems to differ compared to this present work. The difference might be due to the increase in $\theta_{\text{OH}}/\theta_{\text{H}_2\text{O}}$ and $\theta_{\text{H}_2\text{O}}/\theta_{\text{H}}$ at high $a_0$ and high $i$ region, because the higher $i$ at higher $P_{\text{H}_2}$ causes an increase in both $\theta_{\text{OH}}/\theta_{\text{H}_2\text{O}}$ and $\theta_{\text{H}_2\text{O}}/\theta_{\text{H}}$ as shown in Eq. (61). In other words, at a high $a_0$ region, both $\text{OH}_{\text{ads}}$ and $\text{H}_2\text{O}_{\text{ads}}$, which are reaction products of FC, can be a reason for a high overpotential. The coverages of the reactant discussed in previous literature varied, depending on the reaction models and on the procedures used to estimate the coverages. Biberle et al. suggested that $\theta_1$ at 700°C and at OCV was 0.06, and that $\theta$ of other species was smaller [17]. Goodwin et al. [20] and Vogler et al. [22] also discussed the coverages of $\text{O}^\cdot$, $\text{OH}^\cdot$, $\text{H}_2\text{O}$ on YSZ, and $\text{H}$ on Ni and suggested that $\text{O}^\cdot$ almost fully covered YSZ and that $\theta_1$ on Ni was 0.1–0.3 in 700°C at $P_{\text{H}_2} = 0.25$. In those studies, the values of specific coverages depend on the equilibrium constants of adsorption/desorption and on the rate constants of surface chemistry, and those values were substituted with those from literature [19,31,32], and thus the coverages of many of the reactants are independent of the electrode potential. On the other hand, our scheme determines the coverages from the relationship between $i$ and $a_0$ in our data, which is a relationship based on the competitive adsorption equilibrium and can be used to estimate the coverages that depends on $a_0$.

In the present work, even though multiple sets of $K_{\text{H}_2\text{O}}$, $K_{\text{H}_2\text{O}}$, $K_{\text{OH}}$, and $K_{\text{H}}$ were obtained as the optimum by our genetic algorithm and did not be determined as one set, the set of coverages were uniquely determined values by the set of experimental data without any assumptions or preset parameters. While each term in the denominator of Eq. (50) corresponds to the coverage ratio of each reactant and the value of the coverage ratio determines the reaction order, $\theta_{\text{OH}}/\theta_{\text{H}}$ is not a simple term consisting of multiple $K$. In contrast, $\theta_{\text{H}}/\theta_0$, $\theta_{\text{OH}}/\theta_0$, and $\theta_{\text{H}_2\text{O}}/\theta_{\text{H}}$ can be described simply with one $K$, and one experimental parameter. Thus, in order to determine each $K_i$, a machine learning technique, such as a genetic algorithm, is necessary to obtain the global optimum set of multiple parameters. Also required for determination of $\theta$ is a sufficient set of experimental $i$ vs. $a_0$ data including $a_{0(\text{eq})}$ under various $P_{\text{H}_2}$ and $P_{\text{H}_2\text{O}}$. By applying the optimization algorithm and the experimental data set to the reaction model, the intrinsic properties of the electrode material, i.e.,
coverages of reactants, were quantified independently from the effect of the geometric structure of the electrode.

Based on our results with the optimization algorithm and the experimental data, in the reversible SOFC/EC reaction at 900°C, TPB is almost vacant but also partially covered with H2O in P_H2O = 0.01–0.05. Also, at FC reaction with a high i, a large amount of OH was covered with the TPB, but not fully. These properties will be suitable as a reaction field of an FC, because the coverage of TPB is kept sufficiently low. On the other hand, it is not clear that the TPB with Ni/YSZ is suitable for water electrolysis with a high P_H2O, because too high coverage of H2O can inhibit the electrolysis reaction. Further study at a high P_H2O is required to evaluate the effect of θ_H2O. Also, by applying our scheme to determine the coverage of reactant, as shown in Section 3.3, to different electrode materials, porous electrode structures and/or reactant species, the material properties can be directly evaluated. This will promote development of SOFC/ECs. Thus, applying the kinetics model with the optimization by applying the genetic algorithm to the series of data with a sufficient range of gas conditions will be an efficient method to evaluate material properties by using TPB coverages.

### 3.6 Consideration of EC Kinetics by Parameters Determined by FC Reactions

#### 3.6.1 Fitting Results of Reversible FC/EC Reaction

Figure 11 shows superimposed log a_O vs. log i curves fitted by using the nine representative parameter sets of the optimal solution candidate in Table 3, and also shows measured data at both EC and FC regions. Similar to the coverage, every k_a and K_a set represented exactly the same curves. Also, the curves in all four different P_H2O three different P_H2O prepared by one set of k_a and K_a approximately fitted the experimental data at each condition. These results suggest that the kinetics which is governed by the coverage of each adsorbent can be described by Eq. (61) with the constant values of K_122, K_OH_kO2kH^2, and k_aK_H^1/2 with the values shown in 3.4, and that the coverage can be determined as one optimum solution by the genetic algorithm. The experimental data at the SOFC region with 10^-9 < a_O < 10^-8 at different P_H2 and P_H2O was determined in detail by the kinetics equation in each condition. The model curves represent the slope of i vs. a_O, and i/a_O > 1 near the equilibrium and = 1 at an intermediate a_O region.

The model curves at 0.99 P_H2 at 0.01 P_H2O and at 0.97 P_H2O, 0.03 P_H2O were lower than the experimental data, possibly due to the effect of initial degradation of the cell.

Figure 12 shows the I–V and I–P curves, both of which are the same, as shown in Figure 3, but with fitting curves showing the calculated i vs. V or P as Eq. (61). At the FC region, most of the fitting curves, especially at P_H2 = 0.80 (b) and 0.50 (c) at any P_H2O, approximately fit to the experimental data. There are some small gaps between the experimental data and the fitting curves at P_H2 = 0.99–0.97 (Figure 12a) and wide gaps at i > 1.2 A cm^-2 at P_H2O of 0.3 (d). One reason for the wide gaps in the high i region is that MSE as the evaluation index (Eq. (60)) was based on the relationship between log i_exp and log i_calc. Compared using the linear scale i as an evaluation index, the effect of larger i region on the MSE became smaller, thus resulting in the error in the high i region becoming larger to obtain a smaller MSE.

Thus, by obtaining a series of i vs. a_O data that includes the equilibrium potential under different P_H2 and P_H2O in one cell and applying the optimization method with the genetic algorithm, the relationship between a_O and the chemical state of the reactants at TPB, i.e., coverage of reactants at TPB in FC region, can be quantified based on the reaction model. Also, these results suggest that in the FC region with small a_O < 10^-9 the active site of TPB will be almost vacant with a small amount of H2O_ad whereas it is partially covered with OH_ad and H2O_ad at FC region with large a_O > 10^-8.
On the other hand, the model could not determine the relationship between the \( i \) and \( a_0 \) at the EC region with \( a_0 < 1 \times 10^{-10} \). The maximum measured \( i \) at the EC region was 3–6 times larger than that determined by the model at any \( P_{H2O} \) and \( P_{H2} \). The tendencies were observed both in Figures 11 and 12. At lower \( a_0 \), the difference between experimental and calculated \( i \) increases. Assuming that the balance between \( i_a \) and \( i \) is fixed by \( a_{O(eq)} \) in the model and that \( i \) reaches its maximum value, \( i_{(max)} \), at the minimum \( a_0 \approx 0 \) as Eq. (62):

\[
i_{(max)} = \frac{k_n K_H H_2K_OH K_{O(eq)}}{1 + K_{H2O} P_{H2O} + \sqrt{K_{H2O} P_{H2O}}} \tag{62}
\]

In the experimental data as shown in Figure 11, on the other hand, \( i \) continuously increased with decreasing \( \log a_0 \).

### 3.6.2 Possible Modification of Electrolysis Reaction Kinetics

From Eq. (50), \( i \) in the EC region is almost independent of \( a_0 \) because \( a_0 \) is relatively small, but the experimental data shows dependence of \( i \) on \( a_0 \). To describe the relationship between \( i \) and \( a_0 \) in the EC region, another variable that depends on \( a_0 \) is required. Even if the kinetics of electrolysis in Eq. (21) is changed in the model, the equilibrium \( a_{O(eq)} \) limits the balance between \( i_a \) and \( i \). So we reinvestigated the equilibrium of the comprehensive adsorption shown in Eqs. (22) to (24), particularly between \( a_0 \) and \( O_{ad} \) as shown in Eqs. (25) to (27). We assumed the equilibrium of electron activity on Ni and YSZ to be variable (i.e., dependent on \( a_0 \)) and set the electron activity ratio, \( a_e^{YSZ}/a_e^{Ni} \), as another variable. Figure 13 shows schematics of the reaction kinetics and the equilibrium on Ni around TPB in the original model (Figure 13a) and this modified model (Figure 13b). By applying \( a_e^{YSZ}/a_e^{Ni} = f(a_0) \) to the “modified kinetics model” with setting \( a_e^{YSZ}/a_e^{Ni} = 1 \) at the power generation region, the equilibrium between \( a_0 \) and \( O_{ad} \), \( K_{O} \), can be described as in Eqs. (63) and (64):

\[
K_e' = \frac{a_e^{YSZ}}{a_e^{Ni}} = f(a_0) K_e \tag{63}
\]

\[
K_O = K_{O^+} K_{O_{ad}} \left( \frac{a_e^{YSZ}}{a_e^{Ni}} \right)^2 \tag{64}
\]

where \( K_{O} \) is the new equilibrium constant between \( a_e^{YSZ} \) and \( a_e^{Ni} \). Thus, \( i \) is described as in Eqs. (65) and (66):

\[
i = k_n K_H H_2K_OH K_{O(eq)} a_0 \theta_{V}^2 - k_n K_{H2O} P_{H2O} \theta_{V}^2
= k_n K_H H_2K_OH K_{O(eq)} a_0 \theta_{V}^2 - k_n K_{H2O} P_{H2O} \theta_{V}^2 \tag{65}
\]
By this modified equation with this additional independent variable \( \hat{n}_{\text{YSZ}} / \hat{n}_{\text{Ni}} \), \( i = f(\hat{n}_0) \) changes as follows. In the power generation region (e.g., \( \hat{n}_0 > 10^{-3} \)), \( \hat{n}_{\text{YSZ}} / \hat{n}_{\text{Ni}} \) is fixed at 1 and \( i \) in Eqs. (50) and (66) become the same value. In the EC region (e.g., \( \hat{n}_0 < 10^{-3} \)), \( \hat{n}_{\text{YSZ}} / \hat{n}_{\text{Ni}} \) increases when \( \hat{n}_0 \) decreases, and \( i \) also increases although it reaches a constant value in the original model described in Eq. (50).

Figure 14a shows \( i \) vs. \( \hat{n}_0 \) with the curves calculated using the modified model and shows the experimental data at \( P_{\text{H2}} = 0.80 \). Fig. 14(b) shows \( \log \hat{n}_{\text{H2O}} \), \( \theta_{\text{OH}} \), and \( \theta_{\text{H2}} \) dependence on \( \log \hat{n}_0 \) calculated by the original model and by the modified kinetics model at \( P_{\text{H2}} = 0.80 \) and \( P_{\text{H2O}} = 0.03 \). Significant difference appeared in \( \theta_{\text{OH}} \), whereas it linearly decreased with decreasing \( \hat{n}_0 \) in the original model, the gradient became smaller in the electrolysis region in the new model. The \( \hat{n}_{\text{YSZ}} \) on metal is 1, so the electron activity on YSZ increases due to the static charge balance of YSZ near TPB and changes due to the negative voltage. When \( \hat{n}_{\text{YSZ}} / \hat{n}_{\text{Ni}} > 1 \), the equilibrium constant between O(YSZ) and O\(_{\text{ad}}\), as shown in Eq. (24) increases and O\(_{\text{ad}}\) increases at the same \( \hat{n}_0 \). Also, the coverage of OH\(_{\text{ad}}\) increases by the equilibrium Eq. (46). Thus, the O\(_2\) flux can increase and finally the cathodic current can increase.

As a result, the negative charge of YSZ near TPB by applying voltage causes a shift in the equilibrium between O(YSZ), O\(_{\text{ad}}\) and OH\(_{\text{ad}}\), and thus enhances the flux of O\(_2\) at the electrolysis region. Similar phenomena have been discussed as “electrochemical promotion of catalyst (EPOC)” or “non-faradic electrochemical modification of catalytic activity (NEMCA)” effect which occurs on the metal catalysts on the ion conductive oxide support to enhance a catalytic activity of non-faradic reaction by electrochemically modifying the surface ad/desorption equilibrium [48-50]. However, further investigation is needed to confirm our modified EC electrochemical model based on the shift in \( \hat{n}_{\text{YSZ}} / \hat{n}_{\text{Ni}} \). To develop a method to quantify the relationship among O\(_{\text{ad}}\), OH\(_{\text{ad}}\), \( \hat{n}_0 \) and \( \hat{n}_{\text{YSZ}} / \hat{n}_{\text{Ni}} \) in different materials, electrode structures, or temperature, unifying the kinetics model of electrolysis and power generation will be key to establish the methodology to predict the performance of SOECs from that of SOFCs.

4 Conclusions

This study developed a method to quantify the coverage of chemical reactants at TPB by electrochemical measurement to establish a scheme to evaluate electrode materials and structures of SOFC/ECs. In this work, to determine the coverages, (i) a kinetics model based on comprehensive adsorption reaction on a H\(_2\)/H\(_2\)O electrode under the local equilibrium of O\(_2\), O and e\(^-\) in the electrolyte and under the equilibrium between O\(_2\) in YSZ and O\(_{\text{ad}}\) on TPB was applied, (ii) multiple variables including \( k_a \) and \( K_{\text{H2O}}, K_{\text{H2O}}, K_{\text{OH}} \) by machine learning process using a genetic algorithm as the optimization method was developed, and (iii) experimental \( i \) vs. \( \hat{n}_0 \) data was obtained for a reversible SOFC/EC using an electrolyte support cell with YSZ electrolyte and Ni/YSZ H\(_2\)/H\(_2\)O electrode in H\(_2\)/H\(_2\)O/Ar mixture gas. By determining \( K_e \) and \( k_a \), the material properties in the effect of the porous structure of an electrode can be independently discussed. By applying the genetic algorithm, the fitting curve and coverage were uniquely determined for any set of \( k_a \) and \( K_{\text{H2O}}, K_{\text{H2O}}, K_{\text{OH}} \) although numerous optimal parameters were confirmed in the fitting results. As a result, under SOFC conditions, \( \theta_{\text{H2}} \) and \( \theta_{\text{OH}} \) were relatively low, and \( \theta_{\text{OH}} \) was low at oxygen activity (\( \hat{n}_0 \)) < 10\(^{-3}\) and high at \( \hat{n}_0 > 10^{-4}\). When 10\(^{-3}\) < \( \hat{n}_0 < 10^{-3}\), each coverage was 0.94 > \( \theta_{\text{OH}} > 0.35, 0.15 > \theta_{\text{H2O}} > 0.049, 0.022 < \theta_{\text{OH}} < 0.57, \theta_{\text{H2}} > 10^{-4} \) and \( \theta_{\text{H2}} > 10^{-4} \). Finally, one set of \( k_a \) and \( K_a \) approximately described the \( i \) vs. \( \hat{n}_0 \) curves at all of four
$P_{H_2} \times 3 P_{H_2O}$ conditions at SOFC regions. Those result suggests that the active site at TPB under SOFC power generating condition at 900°C is partially covered with $H_2O$ or OH. As for the SOEC, on the other hand, the data showed over 4 times larger $i$ at the electrolysis region compared to that based on our original kinetics model. Therefore, we proposed the modified EC electrochemical model by reconsidering the equilibrium of electrons between YSZ and Ni. In the modified model, another independent variable of the electron activity ratio ($a_{e-YSZ}/a_{e-Ni}$) was applied as a comprehensive electrochemical reaction model of reversible SOFC/ECs. Although further investigation is needed to confirm our modified EC electrochemical model, the results revealed that the increase in cathodic current came from the increased $OH$ coverage ($\theta_{OH}$) due to the shift in local charge balance caused by the increase in $a_{e-YSZ}$.

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List of Symbols

$a_{O}$ Oxygen activity / –
$a_{e-}$ Electron activity / –
$E_a$ Ohmic-free anode potential / V
$E_{a'}$ Ohmic-free anode potential at the potential at the center of electrolyte / V
$F$ Faraday constant = 96,485 A s mol$^{-1}$
$i$ Total current density / A cm$^{-2}$
$i_0$ Exchange current density / A cm$^{-2}$
$i_a$, $i_c$ Anodic and cathodic current density / A cm$^{-2}$
$i_{calc}$ Calculated value of the current density / A cm$^{-2}$
$i_{exp}$ Experimental value of the current density / A cm$^{-2}$
$k_a$, $k_c$ Kinetics constant of anodic and cathodic reaction / –
$K_x$ ($K_{H_2}, K_{H_2O}, K_{O_2}$…) Equilibrium constant / –
$i_{TPB}$ Length of TPB / –
$N$ Total number of experimental data points / –
$O_{x,y}$ Oxygen in YSZ bulk / –
$P_a$ Gas partial pressure / –
$R$ Gas constant = 8.314 J K$^{-1}$ mol$^{-1}$
$T$ Temperature / K
$V$ Potential / V
$V_{ad,y}$ Vacancy on the surface of $y$ active site / –
$V_{O**}$ Oxygen vacancy in YSZ bulk / –

Greek Letters

$\beta_a$, $\beta_c$ Anodic and cathodic symmetric factor / –
$\eta_a$, $\eta_c$ $H_2/H_2O$ and $O_2$ electrode overvoltage / V
$\rho_x$ Electrochemical potential of $x$ / V
$\theta_V$ Vacant active site at TPB / –
$\theta_{x,y}$ Coverage of $x$ on the surface of $y$ at TPB / –

Data Availability Statement

The data that supports the findings of this study are available in the supplementary material of this article.

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