

Spatially and temporally heterothermic kinetic model of hydrogen absorption and desorption in metals with heat transport

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Abstract

Numerical modelling of hydrogen transport is effective for designing and optimizing various energy systems, including hydrogen storage devices, fuel cells, and nuclear fusion reactors. In the present study, we propose and demonstrate a spatiotemporally heterothermic, autonomous kinetic model of hydrogen absorption and desorption in metals for precise simulations. Our bidirectional transport model comprises elementary mass transfer processes of surface adsorption and desorption, subsurface transport, and bulk diffusion. Also implemented are heat generation and conduction stemming from the absorption enthalpy, to determine the evolution of temperature distribution in the metal body, as well as the hydrogen concentration profile. Simulations by our transport model reproduce experimental hydrogen absorption and desorption curves for various temperature levels and metal scales with a single identical set of numerical equations and kinetic parameters, to thus verify the validity of the model.

1. Introduction

Hydrogen storage in metals is an important technology for storing and transporting energy resources, particularly owing to its high volumetric density [1–6]. To efficiently design and optimize the structures and operating conditions of high-performance hydrogen storage devices, systematic understanding and modelling of the kinetics of hydrogen transport on the surface of and inside metals to numerically simulate the absorption and desorption rates for different conditions are essential [7–11]. In a similar context, modelling and consequent controlling of the hydrogenation and dehydrogenation processes of metals are also crucial for the prevention of degradation of structural materials by hydrogen embrittlement [12–14]. Therefore, kinetic modelling of hydrogen transport has been studied for various metals so far [15–19]. To the best of our knowledge, the existing hydrogen absorption and desorption models all handle only mass transport, but do not account for heat generation/dissipation and transport. However, the nature of hydrogen transport essentially reflects heat transport and consequent temperature change in metals. For instance, temperature changes in metals during hydrogen absorption owing to the heat of adsorption and absorption could cause errors in the numerical simulations used to estimate the hydrogen absorption rates, because many kinetic parameters are temperature-sensitive. A kinetic model of hydrogen transport that accounts for heat transport and temperature changes is thus highly demanded for precise numerical simulations. Previously, we developed a numerical model for hydrogen absorption into metals, comprising the kinetics of surface adsorption, subsurface transport, and bulk diffusion, that reflected the relationship between the temperature change in the metal and the temperature-dependent kinetic parameters [20]. Nevertheless, the calculation based on the model used the experimentally monitored temperature of the metal, but not the calculated temperature. Besides, the temperature of the metal was assumed to be uniform throughout the

metal object. In addition, the model was studied only for the hydrogen absorption process, but not for the opposite directional transport of desorption. In the present study, we establish a spatially heterothermic hydrogen transport model in metals, and fully autonomously calculate the time evolution of spatial temperature profile in the metal object via the absorption enthalpy and heat conduction. We further show that our renewed model is valid for both directional hydrogen transport of absorption and desorption, with a single, identical set of formulae and kinetic parameters. An exception, nevertheless, is that our present calculation for hydrogen desorption still requires the monitored temperature due to an incompatibility of the heat balance equations with the necessary forced heating as detailed later, whose dissolution is our future task. Our prototype kinetic model including the subsurface transport of hydrogen and the heat generation and transport could be a basis for numerical simulations with higher accuracy and broader utility over the existing models.

2. Experimental Methods

We employed Pd as a representative hydrogen-absorbing metal in the present experimental study. A flat Pd plate (purity: higher than 99.9 wt%, surface Ra roughness: on the order of 100 nm, Tanaka Kikinzoku Kogyo Corp.) with an areal size of 3 cm × 3 cm was used as a hydrogen-absorbing and -desorbing sample. The thickness of the Pd plate was varied: 0.2, 0.5, 1, and 2 mm. In advance of the measurement of hydrogen absorption and desorption rate in Pd, we annealed the Pd sample at 1000 °C for 10 h in a furnace under a nitrogen atmosphere for the purposes of thorough crystallization, surface degreasing, and native surface oxide removal. The Pd sample is thus considered to have become monocrystalline with strain released. This annealing process was carried out in order to secure experimental reproducibility, by resetting the original processing history at the manufacturer.

We used a homemade Sieverts-type apparatus to measure the hydrogen absorption and desorption rate in Pd in this study. The Pd sample was placed inside the main chamber of the Sieverts-type apparatus, a stainless-steel vacuum chamber with a capacity of $1.6 \times 10^3 \text{ cm}^3$. Figure 1 illustrates the configuration of the experimental system. For hydrogen absorption experiments, the whole apparatus was then evacuated ($\sim 5 \times 10^{-5}$ Torr), and hydrogen gas (purity: higher than 99.999 %, Taiyo Nippon Sanso Corp.) was injected via the reference chamber with a capacity of $1.0 \times 10^3 \text{ cm}^3$ into the main chamber to reach a pressure of 760 Torr. For hydrogen desorption experiments, the Pd sample with a thickness of 1 mm was heated, after full hydrogen absorption at room temperature, 520 Torr, to shift the equilibrium to the desorption mode.

Afterward, the pressure in the chamber gradually decreased (or increased) owing to the absorption (or desorption) of hydrogen into (out of) Pd. The chamber pressure was temporally monitored to determine the real-time hydrogen molar fraction in Pd. Incidentally, in the hydrogen absorption experiments, the hydrogen pressure was observed to decrease to about 700, 640, 520, and 300 Torr for the Pd samples with thicknesses of 0.2, 0.5, 1, and 2 mm, respectively, at the final stage of full hydrogen absorption. In the hydrogen desorption experiments, the hydrogen pressure was observed to increase to about 560 Torr for the Pd samples with a thickness of 1 mm at the final stage of full (equilibrium) hydrogen desorption. The temperature of the Pd sample also changes due to the absorption and desorption enthalpies. To detect this effect of heat, to be incorporated into the measurement and analysis, the temperatures of Pd and gas phase were monitored by using thermocouples. For the accuracy in the measurement of pressure and temperature, the error or fluctuation (noise) was about 1 Torr and 1 °C, respectively. In this manner, the time evolution of the hydrogen absorption and desorption rate in Pd was measured. For some experimental runs, the Pd sample was actively heated using a heater to investigate the temperature dependence of the

hydrogen absorption and desorption rate. The heater power was turned off at the onset of hydrogen absorption experiments, for the ease of using the heat balance model.

3. Theory and Calculation Methods

The basic concept of our numerical model for mass transport is described in Ref. 20 and schematically depicted in Fig. 2. First, gaseous hydrogen molecules dissociatively adsorb to the metal surface sites. The hydrogen atoms migrate from the surface sites to subsurface sites, and eventually into the bulk where they diffuse. The subsurface region locates at the transition from the surface to the bulk of a material. The subsurface typically comprises one or two atomic monolayers lying immediately below the surface, and has a different chemical environment than either the surface or the bulk regions. For metals with high surface activity for the dissociative adsorption of hydrogen molecules, such as Pd and Ti, the hydrogen transport across the subsurface region often becomes the rate-determining process among the elementary transport processes that constitute the entire hydrogen absorption [20,21]. Therefore, it is important to account for the subsurface transport in developing kinetic models for precise simulations of the net transport rates. We formulate the hydrogen mass balances as

$$X_{max} N_s \frac{d\theta}{dt} = J_{ads} - J_{des} - J_{sb} + J_{bs}, \quad (1)$$

$$X_{max} N_s \frac{d\theta_{ss}}{dt} = J_{sb} - J_{bs} - J_{dif}|_{subsurface}, \quad (2)$$

$$\frac{N_b V_b}{A} \frac{dX}{dt} = J_{sb} - J_{bs}. \quad (3)$$

X_{max} is the maximum hydrogen molar fraction in the metal (mol-H/mol-metal). In the present study, X_{max} is set as 1 for Pd [22–26], while X_{max} should be set larger, depending on the metal species, e.g., 3 for Ti [27]. N_s is the molar density of the metal per surface area. θ is the fractional coverage, or occupancy, of hydrogen atoms at the surface. J_{ads} and J_{des} are the hydrogen fluxes for the surface adsorption and desorption processes, respectively. J_{sb} and J_{bs} are the hydrogen fluxes for the inward and outward subsurface transport, respectively. θ_{ss} is the fractional coverage of hydrogen atoms at the subsurface. J_{dif} is the hydrogen flux for the diffusion in the bulk region. N_b is the molar density of the metal per volume. V_b and A are the volume and surface area of the metal, respectively. X [mol-H/mol-metal] is the hydrogen molar fraction in the metal. The values of N_s and N_b are calculated by

$$N_s = \frac{(N_A N_b)^{\frac{2}{3}}}{N_A}, \quad (4)$$

$$N_b = \frac{\rho}{M}, \quad (5)$$

where N_A is the Avogadro constant, ρ is the mass density of the metal, and M is the molar mass of the metal. Consequently, N_s and N_b are $2.8 \times 10^{-5} \text{ mol}\cdot\text{m}^{-2}$ and $1.1 \times 10^5 \text{ mol}\cdot\text{m}^{-3}$, respectively, for Pd [15]. The values of J_{ads} , J_{des} , J_{sb} , J_{bs} , and J_{dif} are determined by [15,16]

$$J_{ads} = 2S(\theta) \frac{P_{H_2}}{\sqrt{2\pi M_{H_2} RT_g}}, \quad (6)$$

$$J_{des} = 2k_{des}^0 (X_{max} N_s)^2 \theta_{HH} \exp\left(-\frac{2E_{des}}{RT_s}\right), \quad (7)$$

$$J_{sb} = k_{sb}^0 X_{max} N_s \theta (1 - \theta_{ss}) \exp\left(-\frac{E_{sb}}{RT_s}\right), \quad (8)$$

$$J_{bs} = k_{bs}^0 X_{max} N_s \theta_{ss} (1 - \theta) \exp\left(-\frac{E_{bs}}{RT_s}\right), \quad (9)$$

$$J_{dif} = D_H^0 \frac{\partial C(z,t)}{\partial z} \exp\left(-\frac{E_{dif}}{RT(z,t)}\right). \quad (10)$$

$S(\theta)$ is the sticking coefficient of hydrogen atoms onto the surface of the metal, to be discussed later. P_{H_2} and M_{H_2} are the partial pressure and molar mass of hydrogen, respectively. R is the ideal gas constant. T_g and T_s are the absolute temperatures of the gas phase and the metal surface, respectively. k_{des}^0 ($4.8 \times 10^{17} \text{ m}^2 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ for Pd [15]), k_{sb}^0 , and k_{bs}^0 are the frequency factors for the surface desorption, and the inward and outward subsurface transport of hydrogen atoms, respectively. θ_{HH} is the probability that two adjacent surface sites are both occupied by hydrogen atoms, which will be discussed later. E_{des} ($4.2 \times 10^4 \text{ J} \cdot \text{mol}^{-1}$ [15]), E_{sb} , E_{bs} , and E_{dif} ($2.2 \times 10^4 \text{ J} \cdot \text{mol}^{-1}$ [16]) are the activation energy values of hydrogen for the surface desorption, inward and outward subsurface transport, and diffusion in the bulk region, respectively. D_H^0 ($2.9 \times 10^{-7} \text{ m}^2 \cdot \text{s}^{-1}$ [16]) is the prefactor of the diffusion coefficient of hydrogen in the metal. $C(z,t)$ is the local concentration of hydrogen in the bulk region. $T(z,t)$ is the local temperature in the bulk region.

Let us describe the details of $S(\theta)$ and θ_{HH} . Two adjacent vacant surface atomic sites are required for the dissociative surface adsorption of hydrogen molecules. Similarly, two adjacent occupied surface sites are required for the recombinative surface desorption of

hydrogen atoms. Therefore, we rigorously account for the locations of the adsorption and desorption sites on the surface, as follows [15,28]:

$$\theta_{OO} = 1 - \theta - \frac{\theta_{OH}}{2}, \quad (11)$$

$$\theta_{HH} = \theta - \frac{\theta_{OH}}{2}, \quad (12)$$

where θ_{OO} and θ_{HH} are the probabilities that two adjacent sites are both vacant or occupied, respectively, and θ_{OH} is the probability that one of two adjacent sites is vacant. Assuming a local quasi-equilibrium among θ_{OO} , θ_{HH} , and θ_{OH} , the following equation has been proposed [15,28]:

$$\frac{4\theta_{OO}\theta_{HH}}{\theta_{OH}^2} = \exp\left(-\frac{E_{eq}}{RT_s}\right), \quad (13)$$

where E_{eq} ($2.1 \times 10^3 \text{ J} \cdot \text{mol}^{-1}$ for Pd [15]) is the energy separation between the site-occupation states. From Eqs. 11–13, θ_{OO} and θ_{HH} can be expressed as:

$$\theta_{OO} = 1 - \theta - \frac{2\theta(1-\theta)}{1 + \sqrt{1 - 4\theta(1-\theta) \left\{ 1 - \exp\left(-\frac{E_{eq}}{RT_s}\right) \right\}}}, \quad (14)$$

$$\theta_{HH} = \theta - \frac{2\theta(1-\theta)}{1 + \sqrt{1 - 4\theta(1-\theta) \left\{ 1 - \exp\left(-\frac{E_{eq}}{RT_s}\right) \right\}}}. \quad (15)$$

Then, $S(\theta)$, which takes into account the hopping of the physisorbed hydrogen molecules at the surface, can be expressed as follows [15,28]:

$$S(\theta) = \frac{S_0}{1 + K \left(\frac{1}{\theta_{oo}} - 1 \right)}, \quad (16)$$

where S_0 is the sticking coefficient for $\theta = 0$, which we set to be 1.0 (dimensionless) [28] in this study, and K (5.0×10^{-2} (dimensionless) [15]) is a constant related to the surface adsorption and desorption. The value of S_0 has little influence on the calculation results in this study because of the subsurface-transport-control or bulk-diffusion-control nature.

To determine the temperature profile in the metal, $T(z,t)$, we formulate heat balances at the surface of the metal:

$$N_b \delta C_p \frac{\partial T_s}{\partial t} = -\Delta H_{abs} (J_{sb} - J_{bs}) - h(T_s - T_g) - \lambda \left. \frac{\partial T(z,t)}{\partial z} \right|_{surface}, \quad (17)$$

and in the bulk region:

$$\frac{\partial T(z,t)}{\partial t} = \frac{\lambda}{N_b C_p} \frac{\partial^2 T(z,t)}{\partial z^2}, \quad (18)$$

where δ is a representative thickness of the surface region, C_p ($26.0 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ for Pd) is the heat capacity of the metal, ΔH_{abs} ($-10 \text{ kJ} \cdot \text{mol}^{-1}$) is the absorption enthalpy of hydrogen into the metal, h is the heat transfer coefficient between the metal and the gas phase, and λ ($71.8 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$) is the thermal conductivity of the metal. Technically, the heat balance of Eq. 17

holds for any δ , but the temperature has to be regarded as constant in the region of the thickness δ . We set δ as 5 μm in this study, accounting for the relatively high thermal conductivity of Pd and the convenience in the computation to circumvent a diverging numerical error of T_s . It is widely known that the initial surface adsorption enthalpy for Pd is about $-50 \text{ kJ}\cdot\text{mol}^{-1}$ and the activation energy for hydrogen diffusion into the bulk region is about $40 \text{ kJ}\cdot\text{mol}^{-1}$, resulting in the net absorption enthalpy, ΔH_{abs} , is about $-10 \text{ kJ}\cdot\text{mol}^{-1}$ [29–31]. For h , we assume a simple dependence on the pressure of gas phase:

$$h = h_0 \frac{P_{H_2}}{P_0}, \quad (19)$$

where h_0 is the heat transfer coefficient for $P_{H_2} = 1 \text{ atm}$, and P_0 is the standard pressure of the gas phase, 1 atm. Figure 3 schematically depicts the basic concept of our numerical model for heat transport.

Eqs. 1–3 are then numerically solved by the finite-difference, forward Euler method, with the update of $C(z)$ and $T(z)$ for each time step, to determine $X(t)$. The shape of the metal is assumed to be a two-dimensional layer with a finite thickness and an infinite area, and the hydrogen transport solely in the direction of the layer thickness is accounted for. Note that V_b/A in Eq. 3 is simply equal to the thickness of the metal plate, which we occasionally vary in this study. The symmetric boundary condition is employed at the central plane of the metal, $z = 0$. This setting is equivalent to the situation where there is no hydrogen flux across the central plane. Hydrogen absorption and desorption from the two outer surfaces of the metal are thus simulated. The values of k_{sb}^0 , k_{bs}^0 , E_{sb} , E_{bs} , and h_0 are to be determined by numerical fitting.

4. Results and Discussion

For $X(t)$ of the experimental data, the amount of substance of the hydrogen gas, n_{H_2} , has to be determined by using T_g via the equation of state. To test the validity of the measured T_g , we here compare the measured T_g and a theoretical T_g in a reference run. For the theoretical T_g , we consider:

$$\frac{P_{H_2} V}{(n_{H_2,0} + \Delta n_{H_2}) T_g} = \frac{P_{H_2,0} V}{n_{H_2,0} T_{g,0}}, \quad (20)$$

from the equation of state, where V is the volume of the gas phase, $n_{H_2,0}$ is the initial amount of substance of the hydrogen gas, Δn_{H_2} is the change in the amount of substance of the hydrogen gas, and $P_{H_2,0}$ is the initial pressure of the hydrogen gas, and $T_{g,0}$ is the initial temperature of the gas phase. Therefore,

$$T_g = \frac{n_{H_2,0}}{n_{H_2,0} + \Delta n_{H_2}} \frac{P_{H_2}}{P_{H_2,0}} T_{g,0}. \quad (21)$$

Meanwhile, the relationship between Δn_{H_2} and the change in X is:

$$(X - X_0) n_{metal} = -2 \Delta n_{H_2}, \quad (22)$$

where X_0 is the initial hydrogen molar fraction in the metal and n_{metal} is the amount of substance of the metal. Therefore, the theoretical T_g is calculated as

$$T_g = \frac{n_{H_2,0}}{n_{H_2,0} - (X - X_0)n_{metal}/2} \frac{P_{H_2}}{P_{H_2,0}} T_{g,0}. \quad (23)$$

The reference run was carried out in a similar manner as the abovementioned hydrogen desorption experiment. The initial values, $n_{H_2,0}$, X_0 , n_{metal} , $P_{H_2,0}$, and $T_{g,0}$ were known at room temperature. The reported equilibrium values of the hydrogen molar fraction were employed for X at each monitored Pd temperature [32]. P_{H_2} was temporally monitored. Figure 4 plots the time evolution of the measured T_g and the theoretical T_g during the intentional increase of T_s in the reference run. As observed, the measured T_g is highly close to the theoretical T_g , and thus our measurement of T_g is thought to be valid, to be used for the calculations hereafter. It is also observed that T_g is relatively close to room temperature even when T_s is well above 100 °C.

Figure 5 presents the time evolution of T_s in the hydrogen absorption experiments with the Pd samples of a 1-mm thickness with varied initial T_s , and the calculated T_s by our numerical model. A sharp increase of T_s is observed immediately after the onset of the hydrogen absorption experiments owing to the initial large flux adsorption of gaseous hydrogen onto the Pd surface, which is well reproduced by our heat transport model calculations. The simplicity of our preliminary heat transport model apparently caused some discrepancy with the experimental data in the intermediate time region, which is to be resolved in our future work. Figure 6 presents the experimental hydrogen absorption curves for the same experimental runs as that of Fig. 5 with varied initial T_s , and the calculated absorption curves by our numerical model. Importantly, we used the calculated $T_s(t)$ by our model, but not the experimentally monitored $T_s(t)$, for the calculations of $X(t)$. In this sense, numerical simulations for hydrogen transport can be autonomously carried out by our model

only by specifying the initial temperature without providing the $T_s(t)$ data. It is observed that our calculation results relatively well reproduce the experimental data of $X(t)$ in the initial and saturation regions, while poorly fit in the intermediate. Through the numerical fitting in Figs. 5 and 6, we determined the fitting parameters as $k_{sb}^0 = 1.5 \times 10^{13} \text{ s}^{-1}$, $k_{bs}^0 = 1.1 \times 10^{12} \text{ s}^{-1}$, $E_{sb} = 5.4 \times 10^4 \text{ J} \cdot \text{mol}^{-1}$, $E_{bs} = 1.8 \times 10^4 \text{ J} \cdot \text{mol}^{-1}$, and $h_0 = 30 \text{ W} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$. Note that these values are not universal among metals, but need to be determined for each hydrogen-absorbing material based on experimental data. Incidentally, we did not use any particular fitting protocol such as the least-square method, but manually fitted by roughly changing the parameters to save our time, since even a single run of our calculation takes an amount of time. As a rule of thumb in our fitting procedure, we firstly roughly determined k_{sb}^0 , k_{bs}^0 , E_{sb} , and E_{bs} by utilizing the property that k_{sb}^0/k_{bs}^0 and $E_{sb}-E_{bs}$ determine the equilibrium X as seen in Eqs. 3, 8, and 9, and subsequently worked for h_0 . It should be noted that our values of E_{sb} and E_{bs} are close to the reported values of $5.6 \times 10^4 \text{ J} \cdot \text{mol}^{-1}$ and $2.2 \times 10^4 \text{ J} \cdot \text{mol}^{-1}$, respectively, by Ref. 16.

So far, we have thus demonstrated that the calculations based on our numerical model reproduce both the experimental data of metal temperature and hydrogen content evolutions for multiple levels of metal temperature, by a single set of equations and kinetic parameters. Next, we vary the scale of the metal body, to further demonstrate the validity of our numerical model of mass and heat transport. Figure 7 presents the time evolution of T_s in the hydrogen absorption experiments with varied Pd thickness, and the calculated T_s by our numerical model. Our model calculations are observed to satisfactorily reproduce the experimental temperature evolution for all the Pd samples of different thicknesses and for the entire region of experimental duration. It is observed that the increase of T_s is larger for thinner Pd samples. This trend is attributed to the fact that the thermal capacity of thinner metal bodies is smaller, while the surface area, which determines the amount of heat

generation, stays the same. Figure 8 presents the experimental hydrogen absorption curves for the same experimental runs as that of Fig. 7 with varied Pd thickness, and the calculated absorption curves by our numerical model. Again, $T_s(t)$ calculated by our model, not the experimentally monitored $T_s(t)$, was used for the calculations of $X(t)$. Lesser agreement of the calculation result with the experimental for thicker Pd samples is observed in Figs. 7 and 8. This trend could be attributed to the neglect of the side facets of the Pd plate for hydrogen and heat transport in our model, whose contribution relatively becomes larger for thicker plates in reality. Therefore, it is important to extend our prototype one-dimensional transport model to fit the structure of hydrogen-absorbing material in each application, for the simulation precision. It is nevertheless observed that each of our calculation results for the specific Pd thickness moderately reproduces each experimental data. Therefore, it is considered that our numerical model of mass and heat transport can respond to the change in the dimension of the metal body.

Let us take a look at the applicability of our numerical model to hydrogen desorption, as well as the hydrogen absorption process we have discussed so far. Figure 9 presents the experimental hydrogen desorption curves with the Pd samples of a 1-mm thickness with varied T_s , and the calculated desorption curves by our numerical model. Note that for the calculations in this desorption part, we had to use the experimentally monitored $T_s(t)$, but not the calculated $T_s(t)$ by our model, because the heat balance represented by Eq. 17 does not hold due to the heat provided by the heater, which was needed to induce hydrogen desorption, as described in the experimental method section. Incidentally, the variation in the initial X , 0.66 – 0.685, is simply due to the difference in the condition of the absorption experiment carried out prior to each desorption experiment. It is observed in Fig. 9 that the calculation result of our numerical model moderately reproduces the experimental data for each Pd temperature. Thus, it is demonstrated that our model can be used for both the directions of

hydrogen transport, i.e., absorption and desorption. Even more remarkably, our model realizes such bidirectional numerical simulations with the same single set of equations and parameters, which also verifies the physical validity of our model.

We have established a numerical model that can simultaneously simulate the hydrogen and temperature profiles in this study. Finally, let us take a look at the distribution of the temperature and hydrogen concentration in the metal. Figures 10 and 11 present the calculated time evolution of $T(z)$ and $C(z)$ profiles in a Pd plate with a thickness of 1 mm, under constant P_{H_2} and T_g of 760 Torr and 20 °C, respectively, in a hydrogen absorption process with $X_0 = 0$, as a general example condition. In Fig. 10, the evolution of the temperature distribution, including the sharp increase at the initial stage due to ΔH_{abs} and the subsequent gradual convergence to T_g , is observed. In Fig 11, the absorption and diffusion of hydrogen from the Pd surfaces towards the middle of the bulk region of the Pd plate are observed. Interestingly, in contrast to the mild gradation of the hydrogen concentration profile, the temperature profile is observed to be highly uniform inside the Pd plate throughout the period. Such a contrast can be attributed to the difference in the intensity of the kinetic parameters for the mass and heat transfer: $4.3 \times 10^{-11} \text{ m}^2 \cdot \text{s}^{-1}$ of the diffusion coefficient $D_H^0 \exp(-E_{dif}/RT)$ in Eq. 10 versus $2.5 \times 10^{-5} \text{ m}^2 \cdot \text{s}^{-1}$ of the thermal transfer coefficient $\lambda/N_b C_p$ in Eq. 18 in the present case.

5. Conclusions

In the present study, we proposed and demonstrated a spatially and temporally heterothermic, autonomous kinetic model of hydrogen absorption and desorption in metals for precise simulations. Our bidirectional transport model comprised elementary mass transfer

processes of surface adsorption and desorption, subsurface transport, and bulk diffusion. Additionally implemented were heat generation and conduction stemming from the absorption enthalpy, to determine the evolution of temperature distribution in the metal body, as well as the hydrogen concentration profile. Simulations by our transport model reproduced experimental hydrogen absorption and desorption curves for various temperature levels and metal scales with a single identical set of numerical equations and kinetic parameters. Furthermore, our calculations reproduced the time evolution of temperature of the metal for a variety of conditions. In this manner, the validity of our numerical model was verified. The bidirectional hydrogen transport model with a combination of mass and heat transfer may be an effective tool for designing and optimizing various energy systems, such as hydrogen storage devices, fuel cells, and nuclear fusion reactors. So far, our model is for one-dimensional transport in a single flat metal body, since we employed plate-shape Pd samples for the convenience of our experiment and analysis in the present work. For spherical metal particles, as many of the practical hydrogen storage materials, one can simply replace Eq. 10 with the polar-coordinate form of the diffusion equation [33], as we calculated in Refs. 20 and 21. As we observed smaller agreement of the calculation result with the experimental for thicker Pd plates, for instance, it is important to account for the contribution of the side facets to hydrogen and heat transport. We are going to extend our model for higher-dimensional, complex shapes for broader applicability in our future study.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Figure Captions

Fig. 1 Schematic illustration of the configuration of the experimental system.

Fig. 2 Conceptual schematic diagram of our calculation model for hydrogen transport in metal. J_{ads} and J_{des} are the hydrogen fluxes for the surface adsorption and desorption processes, respectively; J_{sb} and J_{bs} are the fluxes for the migration of hydrogen from the surface to the subsurface, and from the subsurface to the surface, respectively; J_{dif} is the hydrogen flux for diffusion in the bulk region; and θ and θ_s are the fractional coverages at the surface and subsurface, respectively. Reprinted with permission from Ref. 21. Copyright 2020 Elsevier.

Fig. 3 Conceptual schematic diagram of our calculation model for heat transport. T_g and T_s are the absolute temperatures of the gas phase and the metal surface, respectively; $T(z)$ is the temperature profile in the metal; J_{sb} and J_{bs} are the fluxes for the migration of hydrogen from the surface to the subsurface, and from the subsurface to the surface, respectively; q_{trans} is the heat transfer flux between the gas phase and the metal surface, $h(T_s - T_g)$, where h is the heat transfer coefficient; q_{cond} is the heat conduction flux in the metal, $-\lambda \partial T(z) / \partial z$, where λ is the thermal conductivity.

Fig. 4 Time evolution of the measured T_g and the theoretical T_g during the intentional increase of T_s in the reference run.

Fig. 5 Time evolution of T_s in the hydrogen absorption experiments with the Pd samples of a 1-mm thickness with varied initial T_s , and the calculated T_s by our numerical model.

Fig. 6 Experimental hydrogen absorption curves with the Pd samples of a 1-mm thickness with varied initial T_s , and the calculated absorption curves by our numerical model.

Fig. 7 Time evolution of T_s in the hydrogen absorption experiments with varied Pd thickness, and the calculated T_s by our numerical model.

Fig. 8 Experimental hydrogen absorption curves with varied Pd thickness, and the calculated absorption curves by our numerical model.

Fig. 9 Experimental hydrogen desorption curves with the Pd samples of a 1-mm thickness with varied T_s , and the calculated desorption curves by our numerical model.

Fig. 10 Calculated time evolution of $T(z)$ profile in a Pd plate with a thickness of 1 mm, under constant P_{H_2} and T_g of 760 Torr and 20 °C, respectively, in a hydrogen absorption process with $X_0 = 0$.

Fig. 11 Calculated time evolution of $C(z)$ profile in a Pd plate with a thickness of 1 mm, under constant P_{H_2} and T_g of 760 Torr and 20 °C, respectively, in a hydrogen absorption process with $X_0 = 0$.

Figures

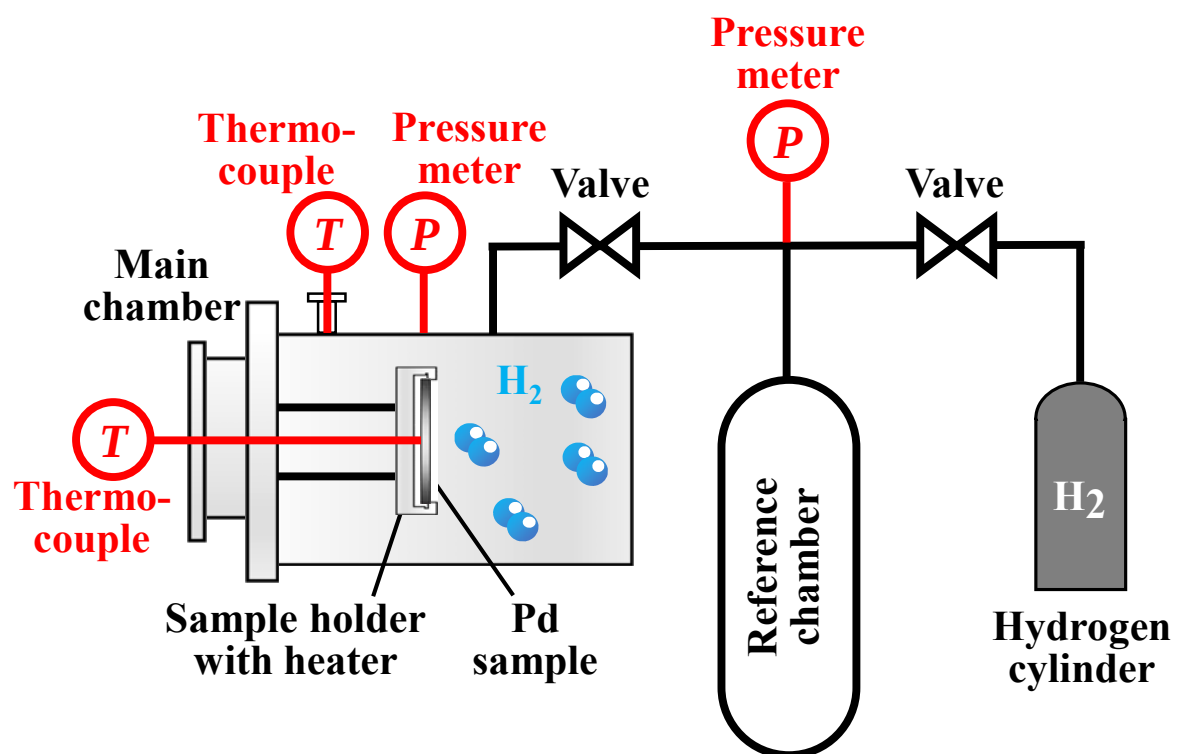


Fig. 1

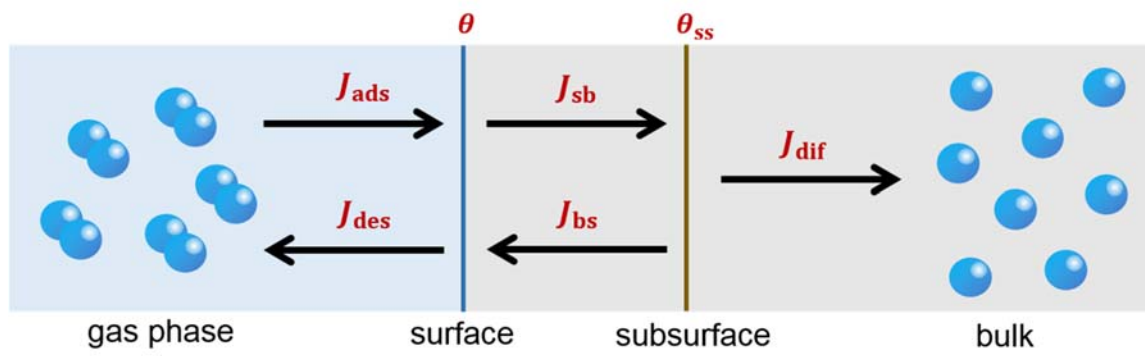


Fig. 2

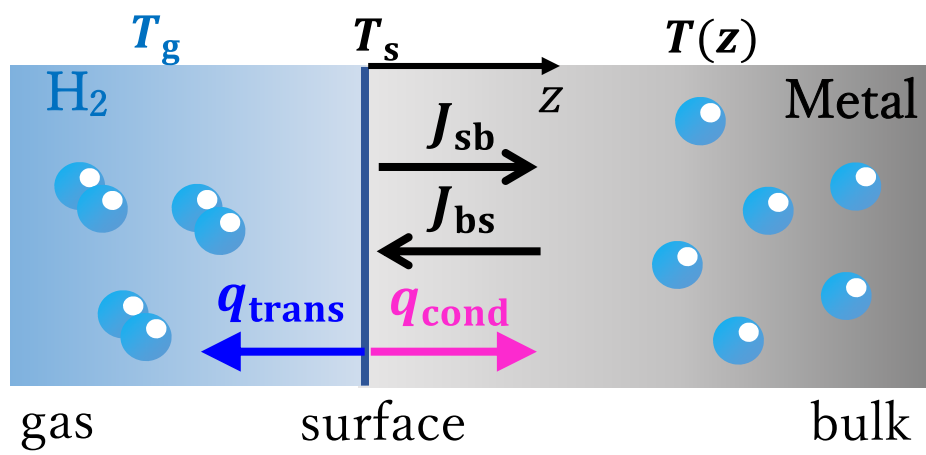


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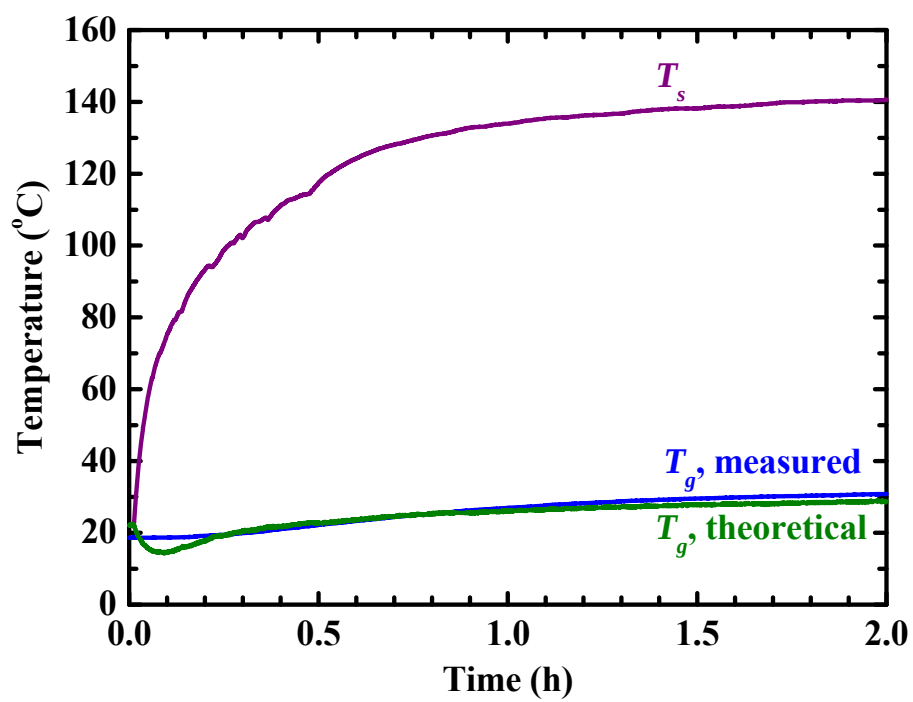


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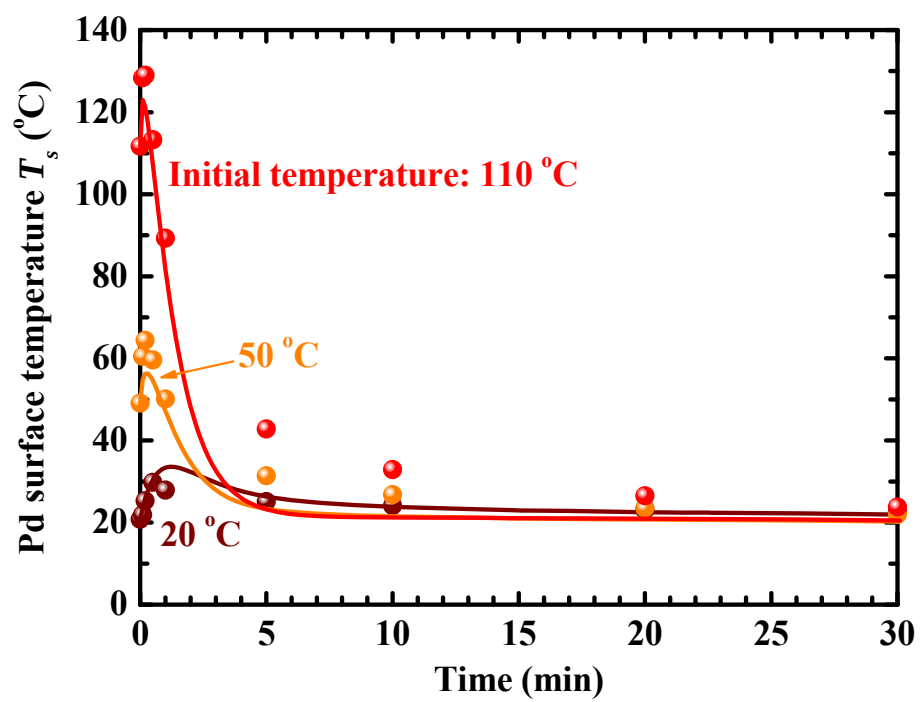


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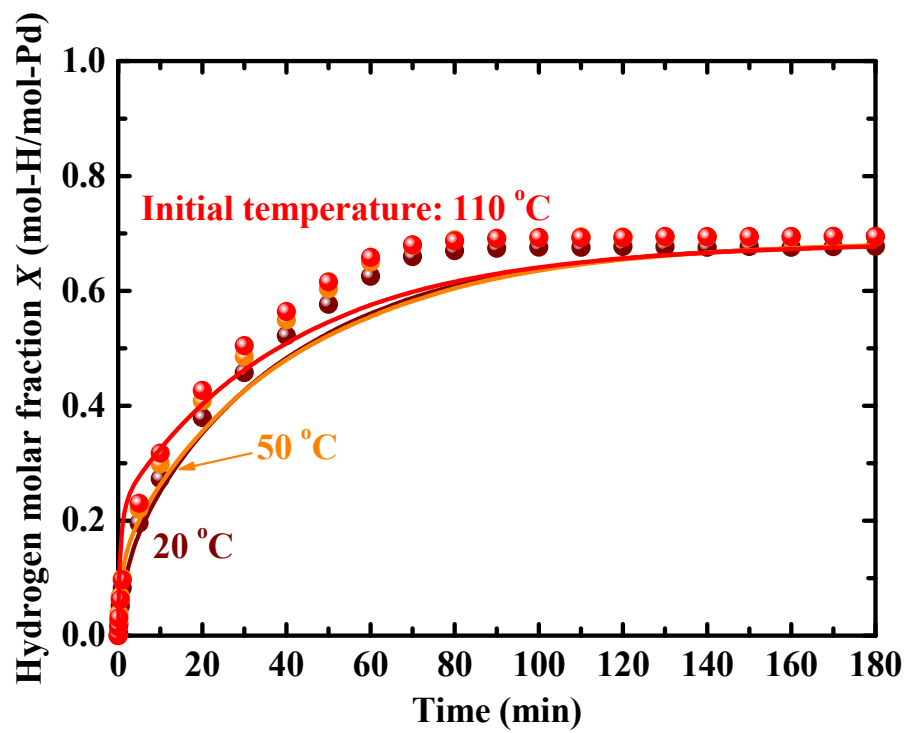


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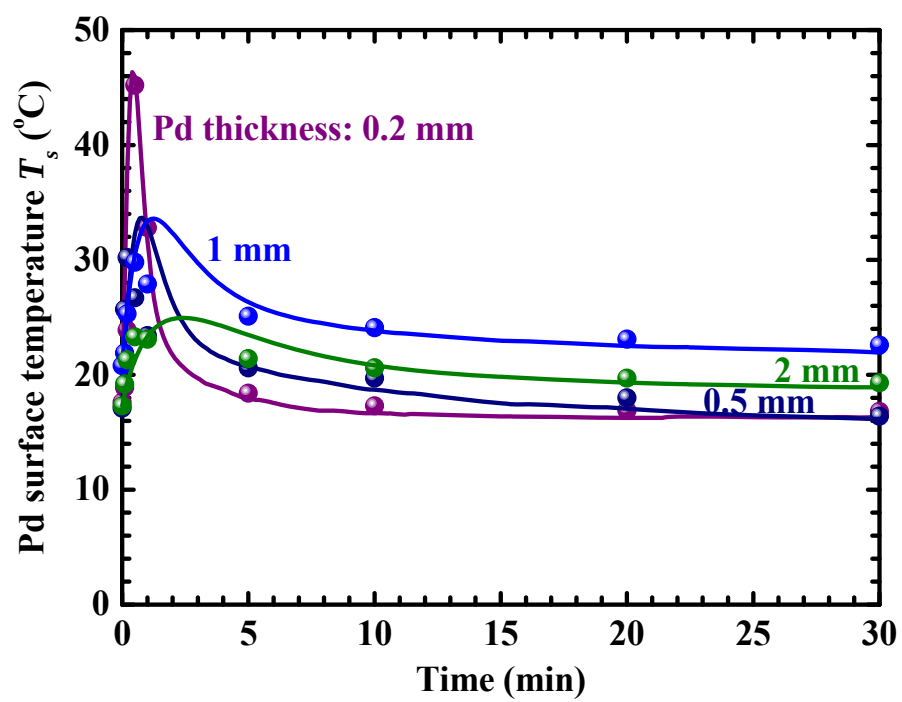


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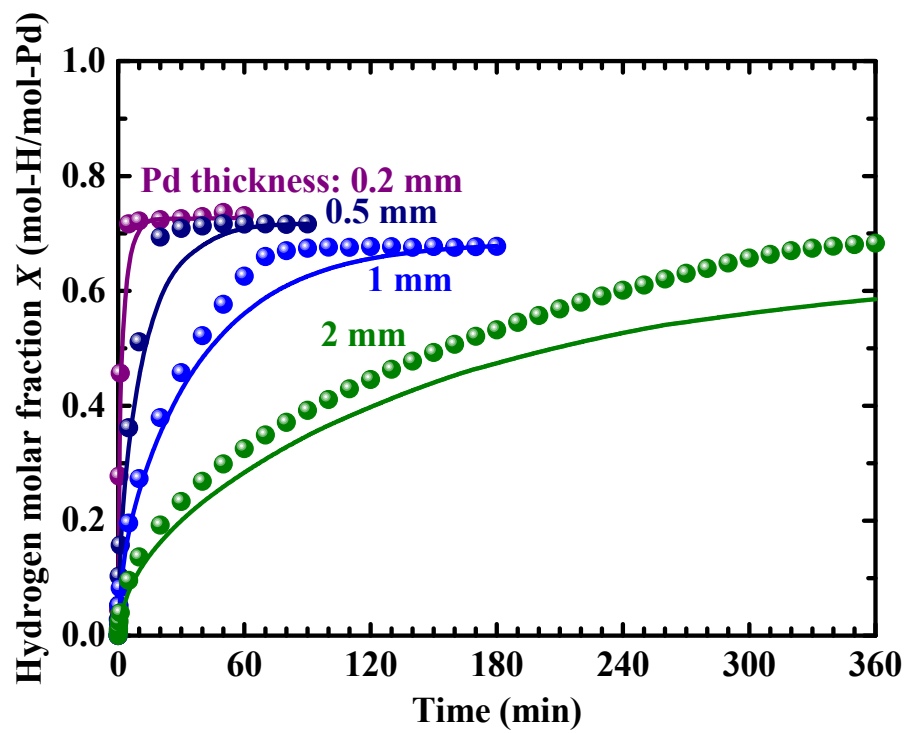


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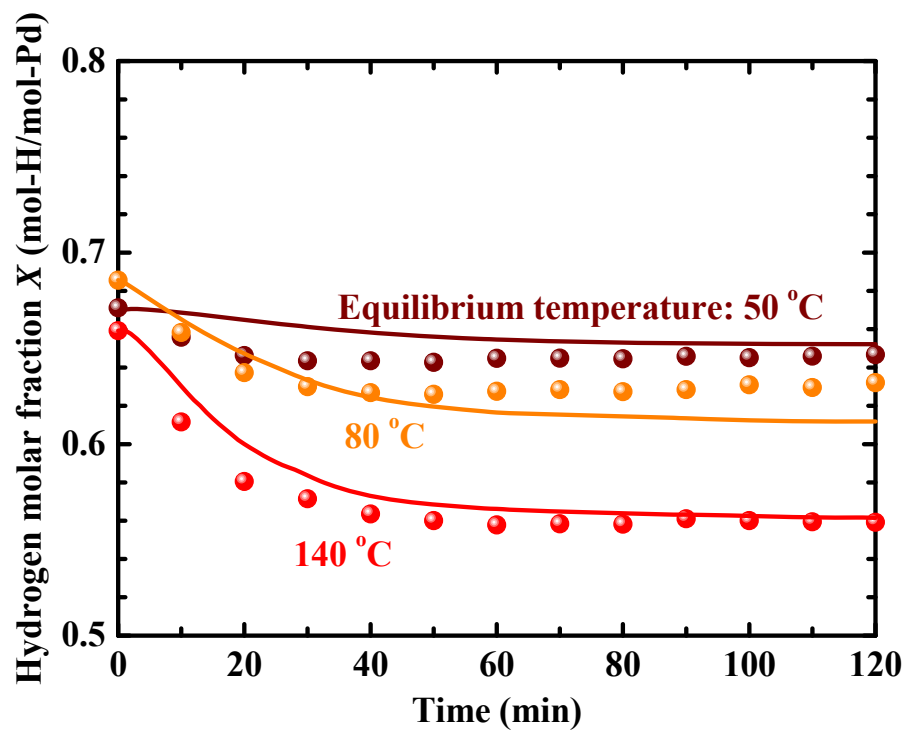


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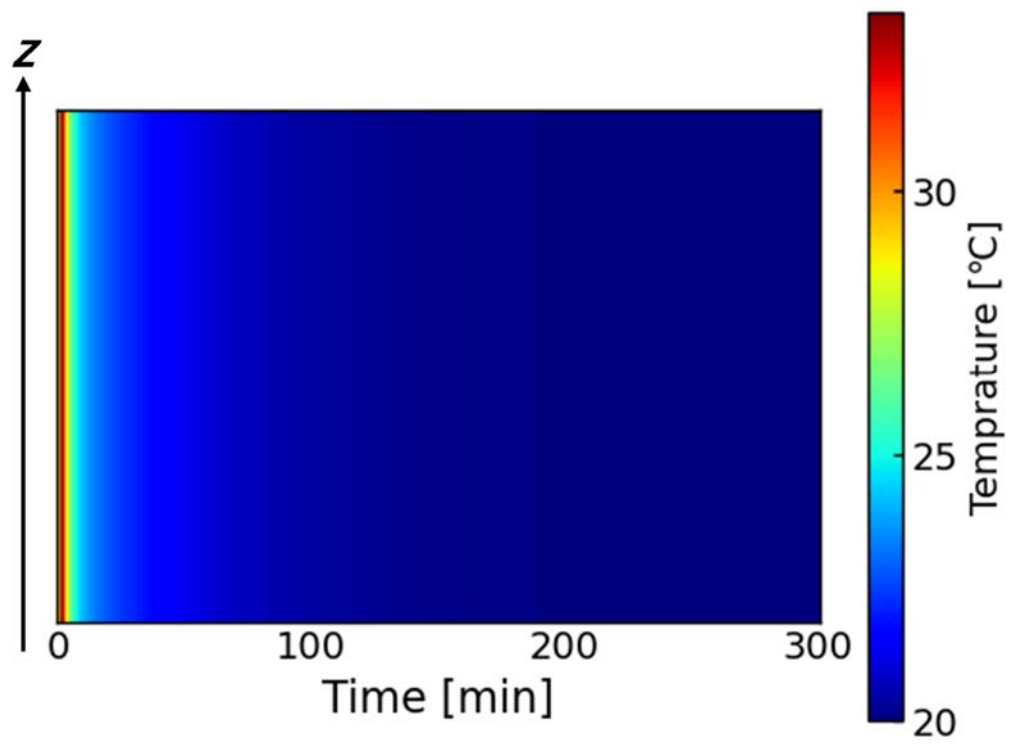


Fig. 10

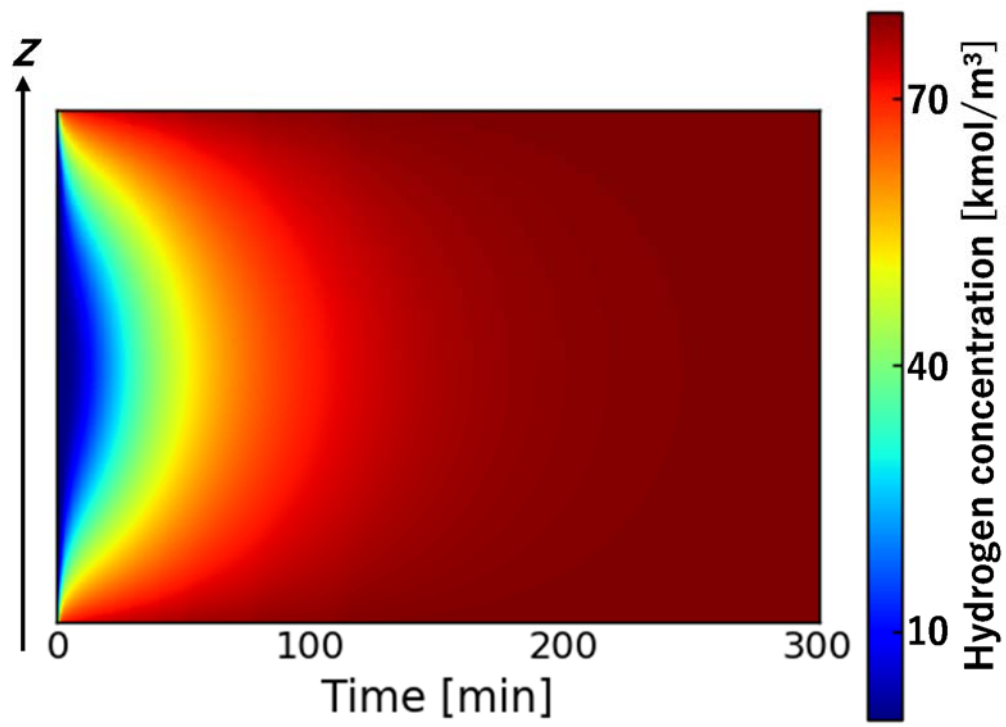


Fig. 11