Application and Management of Hydrogen Energy Technology Toward the Solar Cell Based Distributed Electricity Grid

太陽光発電を主力とする分散グリッド実現のための水素技術の導入，制御法の検討

Kei HASEGAWA

長谷川 馨

The renewable energy-based energy mix is strongly desired, but the gap between the electricity demand/supply will increase, so the energy storage in a distributed grid is expected as key technologies. At the same time, the technology to forecast and control the demand/supply are also required. Based on these two research works, the availability of the hydrogen energy storage and the technological issues were discussed. By using annual, 1-min resolution energy data in the smart energy system "ENE-Swallow" which is applied in Tokyo Institute of Technology, the energy balance in the future distributed grid with a large-scale solar cell was estimated. Also, based on the solid oxide fuel cell kinetics model on triple phase boundary, the comprehensive model of reversible fuel cell / electrolysis is discussed to predict the electrolysis performance from that of the fuel cell.

再生可能エネルギーの主力電源化が強く求められる中，増大する需要－供給ギャップを制御するための蓄エネルギーの分散グリッドへの導入が期待されている。また，電力需要，供給の変動が複雑化するため，その予測，制御技術の革新も必須である。本研究は水素蓄エネルギーに関する2研究のもと，分散システムへの導入可能性と課題を議論した。東工大で運用されているスマートシステム「エネスワロー」に蓄積される年間，1分ごとのデータを用い，太陽電池が大量に導入された想定での水素蓄エネルギーの導入評価を行った。また，固体酸化物燃料電池の反応速度モデルの電解反応への適用可能性を評価し，燃料電池の知見の電解反応への活用を検討した。

Introduction

A challenging target of CO_2 emission reduction in japan as 26% until 2030 and 80% until 2050 have settled under the Paris Agreement at COP 21. To achieve the target, almost zero-emission is required in the electricity supply and the renewable energy based energy mix and the shift to hydrogen society is strongly desired.[1] At the same time, the installation of the renewable energy, especially the solar power generation, rapidly increasing due to the rapid cost reduction in the last ten years. On the other hand, to keep their installation rate of variable renewable energy (VRE), the development of the distributed grid is a key role, but the increase of both of the temporal and positional gap between the electricity demand and supply will be a critical issue. Solar cell works only daytime and the power generation decreases significantly at the evening, so the daily profiles of the gap between the

electricity supply and demand becomes a shape so-called "duck curve"[2] and the matching the electricity demand[*1] and supply by the power grid such as controlling the output of thermal power generation or using pumped-power generation becomes a hard work. So the desired amount of energy conversion, transport and storage expands and the hydrogen related technologies are expected as one of the key technologies. At the same time, the demand/supply gap becomes complicated and hard to predict in distributed grids because of their smaller scale, so further development for the forecasting and managing technology is necessary. Both the power supply by VRE and the human behavior are strongly related to the local climate or the weather, especially on the future distributed grid in the urban area, a part of the energy supply and demand has a strong relationship between each other in the local area. Thus, (1) to develop each elemental technologies under the scientific basis, (2) to establish the total

system to manage each device under the unsteady conditions and (3) to develop the technology to forecast and control the electricity demand/supply with closely relating each other are all required and the comprehensive discussion under the sufficient understanding of each other elements is also necessary.

*1: Matching the electricity demand and supply: the electricity suppliers are obligated to feed the power with a stable voltage to avoid the blackout and the damage for electrical appliances. They keep the voltage in a certain range by forecasting the electricity demand and control the amount of electricity supply.

Under the Global Hydrogen Energy Unit in Tokyo institute of Technology, a total scenario investigative research of the development of hydrogen related technologies are carried out and discussed the availability of the hydrogen energy, the future scenario to solve the technological issues.[1] In the investigation we studied the following two topics which is relating to the hydrogen technology for energy storage in the distributed energy system. One is the evaluation of the applicability of hydrogen energy storage into the distributed system based on the real data. Another is the prediction of the future development of solid oxide fuel cell/ electrolysis (SOFC/EC) based on the scientific discussion and the trend analysis. By those two different approaches based on the real data in the distributed energy system and the device performance based on the scientific basis, the availability of the "local hydrogen" as the energy storage to utilize VRE in the distributed energy system, the issues to install and control the system and the development scenario are discussed.

Research 1: evaluation of the applicability of hydrogen energy storage into the distributed system based on the real data

In order to supply electricity with the stable voltage under the unsteady demand, the central power grid suppliers have controlled the power generation output under a certain empirical forecast of the demand. The recent significant increase of VRE installation makes these situation more complicated. Figure 1 shows an electricity supply and demand curve in a sunny day in autumn, 2017 in Kyusyu area (the graphs were drawn from the ref.[3]). Because the solar power generation (the cells which is not connected to the grids are not counted) reaches over 70% of total demand in daytime at maximum, the supply controlled by saving the output of thermal power generators ant using the pumped-power generators and finally a certain amount of solar power is also curtailed. In such a situation, to take some role balancing between electricity supply and demand in the distributed grids with applying and using some energy storage technology will be a key to the continuous VRE installation in the society. While the electrochemical energy conversion such as secondary battery is a strong candidate for the energy storage, hydrogen energy storage with fuel cell and water electrolysis is considered with their advantage for the energy storage with a longer time and the lower system cost. Many research groups have been evaluated the feasibility of the energy storage in the both the central and the distributed grid,[4, 5] but the number of studies which investigates the future situation with a larger VRE installation ratio such as over 30% is limited. The required amount of the energy storage devices and their frequency of their usage will be totally different, so the discussion with using the annual data will be important.

By considering the distributed grid with 10,000 kW electricity demand and a large scale VRE and evaluate the applicability of installing and utilizing the hydrogen energy storage system to equalize the supply/demand balance, the key factor (or the key technology necessary to develop in the near future) to optimize the total system is discussed. In this study, we estimated the future scenario with a large amount of solar cell installation in the
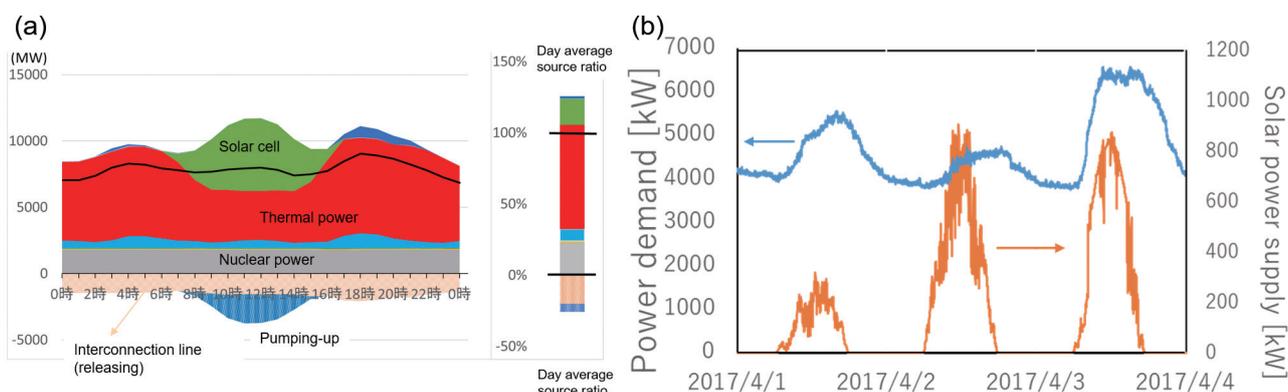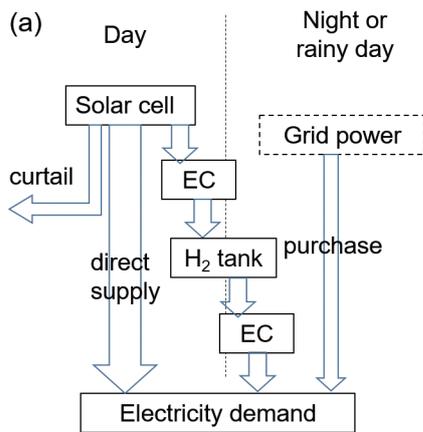

Figure 1 (a) A daily profile of the electricity demand (black line) and the supplies on a fall sunny day in 2017. The graph are made from the open data by Kyusyu Electric Power Co.[3] (b) The profiles of the electricity demand and solar power generation in a few day at Oookayama Campus, Tokyo Institute of Technology. The data were stored by "ENE-Swallow".

distributed grid which makes more difficult to manage the balance between the electricity supply and demand. In the local distributed grid, the time profile of both the electricity demand and supply varies and directly depends on the environmental condition and human behavior, so the investigation based on the real data in the distributed system is required. In Oookayama campus, Tokyo Institute of Technology, a smart energy system "ENE-Swallow" which is developed by Prof. Ihara et al. installed and is managing the energy supply (including 1,400 kW solar cells) and demand (10,000 kW at maximum). Also, in Energy and Environment Innovation (EEI) Building,

650 kW solar cell, 100 kW fuel cell, 70 kW gas engine and 100 kWh lithium ion batteries are installed and the CO_2 emissions are saved into 40%. In "Ene-Swallow", the annual and data of the energy supply by each devices and the demand of each facility are stored in 1 s~1 min resolutions. Figure 1b shows examples of the electricity demand and solar power generation data in a few days with a 1 min resolution in Oookayama campus. Both data, especially the solar power, largely scattered (seemed to be randomly) depends on the environment and/or the human behavior. By using the real data, we estimated the energy supply/demand balance in the future distributed grid with a large-scale VRE and discussed the feasibility of the local hydrogen energy storage system in the grid.

We assumed a distributed grid with a 10,000 kW maximum energy demand and a large installation ratio of solar cell (> 60% of the demand) and the hydrogen energy storage system composed of the fuel cell (FC), electrolysis (EC), hydrogen tank and compressor. Annual data of electricity demand and solqar power generation at April, 2016 ~ March, 2017 was used for the investigation. The total energy system is considered as shown in Figure 2a and the parameters of each device at the 2030s were collected as shown in Figure 2b.[2, 6-9] The self-sufficient ratio by solar cell (= photovoltaic, PV) was set as 60-100% by changing the PV installation ratio as 100% to 190% vs. total demand and estimated the total system cost at different installation ratio of FC and EC by calculating the required hydrogen tank and the purchase of electricity and integrating the annual required amount of hydrogen and electricity curtailment.

Figure 3a, 3b shows the total electricity price including the system cost and the purchased electricity at at 100% PV installation ratio (a) and 190% and at different EC installation ratio. As a result, in some case with the device cost at the 2030s, installing a certain amount of hydrogen energy storage can reduce the total electricity cost at both

(a)

Device	Price (¥/W)	Lifetime (Year)	Efficiency (HHV)
PV	70	30	
EC (Alkaline)	70	10	0.8
FC (SOFC)	105	20	0.65
H_2 tank (45 Mpa)	6,000 (¥/L)	20	4 (kg-H_2/¥)
Compressor	200,000 (Nm³/h)	20	
Purchase electricity price from grid	21 (¥/kWh)		

Figure 2 (a) The assumed distributed energy system with hydrogen energy storage in the study. (b) The technology parameter sets of devices in the near future (about 2030s).
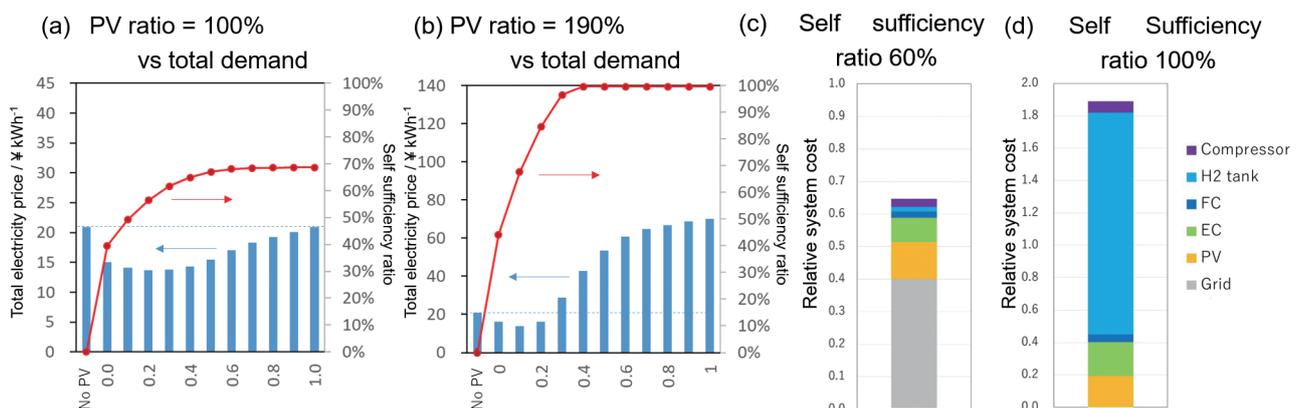
Figure 3 (a)(b) The calculated electricity price and the self sufficiency ratio in the distributed system with different EC installation ratio at PV ratio of 100% vs. total demand (a) and 190% (b). (c)(d) The cost details at 60% self sufficiency (c) and 100% (d).

case. At the PV installation ratio is 100%, the total electricity cost decreased but the maximum self sufficiency ratio reaches less than 70%. On the other hand, to achieve the self sufficiency ratio as 100%, PV installation ratio is needed to be > 190% because of the energy conversion efficiency of FC and EC, and a large amount of hydrogen tank was required as shown in Figure 3c, 3d. By analyzing the seasonal tendency of the hydrogen in the tank, they worked only one time a year to solve the seasonal (= long time scale) supply/demand gaps and their low frequency of usage made them higher cost. The cost reduction of hydrogen generating facilities such as EC, tank or compressor are supposed to be desired and the total management strategy not only the energy storage itself should be discussed. Our total scenario investigations are ongoing including the topics of the effects of the installation amount and the setting angles of solar cell, consideration of future electricity market or the contribution for the leveling of the electricity supply in the grid.

Research 2: investigation of comprehensive kinetics model of reversible solid oxide fuel cell / electrolysis with competitive adsorption reaction on anode triple phase boundary

SOFC has developed for a large-scale energy conversion device for a long time due to their high efficiency, low material cost and fuel flexibility due to their high operation temperature. SOFC has similar advantages and so it is promising for the hydrogen generation from renewable power source and for distributed energy system to equalize the local unsteady power source. Under the situation, the followability and durability under the unsteady conditions with keeping the energy efficiency are required to follow the gap between the electricity demand and the supply in addition to the maximum hydrogen productivity and efficiency. To achieve those properties, the quantitative understanding of the reaction kinetics at wide range of the operating conditions. Especially, electrolysis is an endothermic reaction with a certain exothermic heat loss, so the appropriate reaction control with keeping the heat balance is required to avoid the damage to the cell materials and to keep the efficiency. Whereas SOFC science and technology have well developed for a past several decades, there are limited number of studies which are specialized in development of SOEC.[10-12] Because the requirement of electrolysis technology rapidly expanding in a few years, to learn from the knowledge in the SOFC research field is important to accelerate the development of SOEC science and technology and to develop the way to extrapolate the rate of EC from that of FC reaction is required.

To develop the comprehensive kinetic model of reversible reaction, to describe the reaction kinetics on the triple phase boundary[*2] (TPB) is necessary. The large overvoltage is required for the reaction of hydrogen and oxygen on the TPB of fuel electrode in SOFC, so the reaction in fuel electrode is the key to establish the comprehensive model of SOEC/FC. To discuss the reaction kinetics on TPB, there are two major group when we focus on the rate determining step. One is the reaction across TPB between the surface of oxide and the metal with the charge transfer and the relationship between the current, i, and overpotential, η, is described as Butler-Volmer equation [13-15]. Biebelre et al., suggested the reaction as "hydrogen spillover" [13]. Another kinetics model is the rate determining step as a chemical reaction of the surface adsorbents under the local equilibrium of charge transfer reaction and is described as a kinetics equations of surface chemistry [16-18]. Mizusaki et al proposed the reaction kinetics under the local equilibrium of charge transfer [16]. Based on that local charge transfer equilibrium, our research group proposed the kinetics model with the competitive adsorption reaction which is described as a Langmuir-type kinetics equation [18]. In any models, while the rate of electrolysis has been assumed as the reversible reaction of hydrogen oxidation reaction or a different reaction, the quantitative understanding of the relationship between FC and EC reaction have not been developed yet.

*2: Triple phase boundary (TPB): the interface between (1) gas, (2) oxide as ion conductor and (3) metal electron conductor. The electrochemical reaction proceeds on the interface by these three reactants and how to organize the structure is the key technology in the electrochemical energy conversion devices.

In this work, the reversible reaction was discussed based on our reaction model on TPB and a series of reversible SOFC/EC data. The oxygen activity at the TPB, a_O, is calculated from Ormic-free Ea which the derivation process is shown below as:

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

where F is Faraday constant, E_a= anode potential ($E_a = \Delta V_{terminal} + \Delta V_{ohmic} + \eta_c$ where $\Delta V_{terminal}$ is terminal voltage, ΔV_{ohmic} is ohmic loss and η_c is cathode overvoltage), R is gas constant and T is temperature. The experimental cell was composed of the four electrodes with anode working (AW), anode reference (AR), cathode working (CW) and cathode reference (CR) on the electrolyte as shown in Figure 4a, photograph and the cross sectional SEM image are shown in Figure 4b and c and the Ormic-free E_a is measured the potential difference between AW and CR by current interruption method as shown in
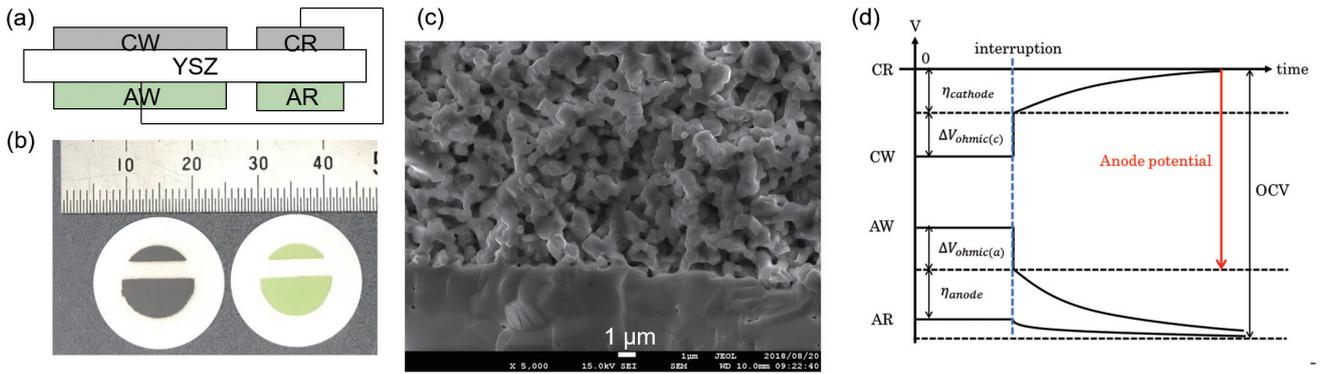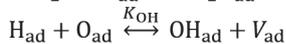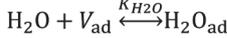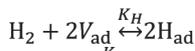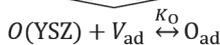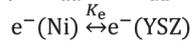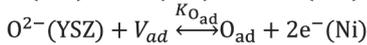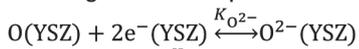
Figure 4 The image (a) and photographs (b) of a four electrode SOFC/EC cell. (c) Cross sectional SEM image of porous anode on YSZ electrolyte. (d) The image of current interruption method in order to measure anode potential, E_a.

Figure 5 The chemical (up left), electrochemical (down left) equilibrium and the relationship between equilibrium constant and the surface coverages on TPB in the kinetics model.

Figure 4d. The chemical and electrochemical equilibrium on TPB is described as shown in Figure 5 and the rate determining reaction can be described as follows where i is current, ia and ic is anodic and cathodic current, k is rate constant and θ is surface coverage on TPB.

$$i = i_a - i_c = k_a\theta_H\theta_{OH} - k_c\theta_{H2O}\theta_V \quad \cdots\cdots\cdots\cdots (2)$$

As a result, the reaction rate is described as the equation.

$$i$$
$$= \frac{k_{a2}K_H P_{H2} K_{OH1} K_O a_O}{(1 + K_O a_O + \sqrt{K_H P_{H2}} + K_{H2O}P_{H2O} + K_{OH1}K_O a_O\sqrt{K_H P_{H2}})^2}$$
$$- \frac{k_{c2}K_H P_{H2O}}{(1 + K_O a_O + \sqrt{K_H P_{H2}} + K_{H2O}P_{H2O} + K_{OH1}K_O a_O\sqrt{K_H P_{H2}})^2}$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (3)$$

The coverages of each species are determined by a_O, and the local equilibrium state between gas phase and Ni surface nearby TPB. The model is composed of the rate of Langmuir reaction determined by the TPB length depends on the porous electrode structure and the coverage of each

species on Ni nearby TPB that is independent on the electrode structure. We confirmed validity of the model in SOEC reaction by applying it to the SOFC/EC reaction with a series of gas conditions on the electrode with well-defined structure composed of a cermet anode by nickel (Ni)/yttria stabilized zirconia (YSZ) which is the most commonly used.

The calculation flowchart is shown in Figure 6a. After considering the a_O at equilibrium, the equilibrium constant, K_x, were determined by the nominal reaction order vs. a_O, P_{H2O} or P_{H2}. Finally, the k was determined by the fitting to the experimental data. Figure 6b, 6c shows the experimental data and the calculation curves of the FC/EC data at the different P_{H2O} and P_{H2}. Much higher current than the model was observed at electrolysis mode at each conditions whereas the model reproduced well at power generation mode. In the model as shown in Equation 3, the electrolysis current becomes constant when a_O is sufficiently low, but those continuously increased in the experimental data. Thus, the kinetics of electrolysis reaction is required to be reinvestigated, so we reestablished the kinetic model by considering the local equilibrium of adsorbents, ion and electron nearby TPB.

By considering the local equilibrium of charge transfer reaction of oxygen as shown in Figure 5, the balance of the charge on the Ni and YSZ, the relative electron activity in other words, can be a key to the electrolysis current. It supposes that the negative charge of YSZ around TPB by applying voltage cause the shift of equilibrium between O(YSZ) and O_{ad} and it enhance 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-faradaic reaction by
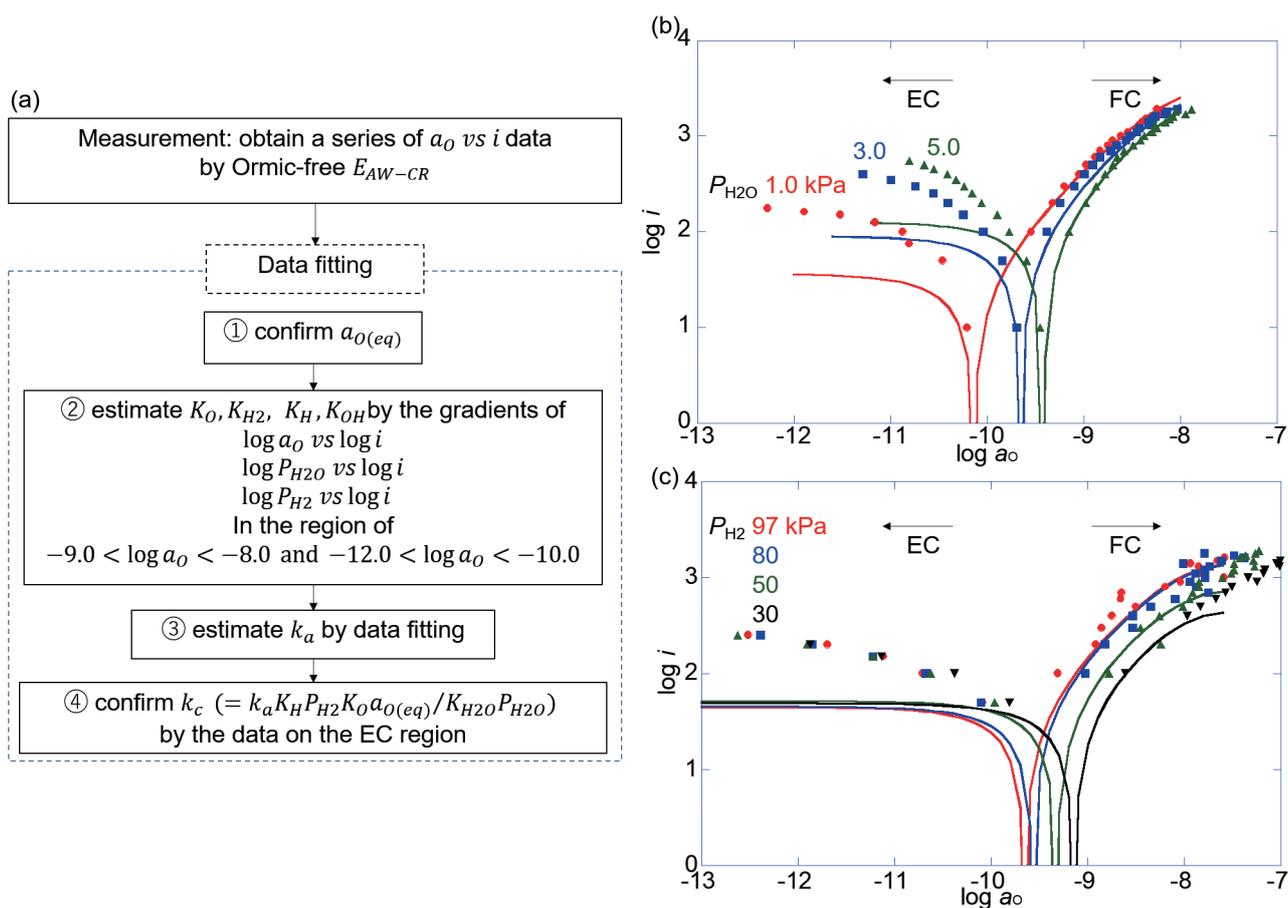
Figure 6 (a) The process flow to calculate the relationship between a_O and i. (b) The experimental data (dots) and the calculated curves (lines) of a_O vs. i at different P_{H2O} and P_{H2}.

electrochemically modifying the surface ad/desorption equilibrium.[19, 20] To develop the way to quantify the relationship between O_{ad}, a_O and the relative electron activity in different material, electrode structure or temperature and to unify the kinetic model of electrolysis and power generation will be key to establish the methodology to predict the performance of SOEC from that of SOFC. In addition, when the desirable SOEC performance is predicted by using the top data of SOFC in the literature, over 5 times higher rate is supposed to be achieved compared to the previously reported values. To achieve such a high productivity of hydrogen and apply the reversible SOFC/EC for the energy storage, further theoretical and experimental studies will be necessary.

Discussion

In the first research topic, by using the real data in "ENE-Swallow", we estimated the local hydrogen storage at the future distributed energy system with large amount of VRE installation. By a rough estimation, a surplus power by solar cells occurs at most of the sunny day if their installation ratio is over 10% of the total demand, and the surplus power becomes severe problem for the further installation of solar cell without the sufficient energy

storage. Thus, to establish the strategy for applying and managing the sufficient amount of energy storage system is an urgent issue (= not the future research topic) to avoid the suppression of the VRE installation into the society. In our study, a certain positive effect of the hydrogen energy storage system to the distributed system with 60% or 100% self-sufficiency ratio by the solar cells. On the other hand, there are some issues to install the sufficient amount of hydrogen system. One is the seasonal value of the solar power generation and the demand which influences to the usage frequency of the hydrogen tank and causes its severe cost increase. To solve the issue, to consider not only the development of the hydrogen storage system itself but also the total system is important including the installation way of solar cells, utilize the future variable electricity market and/or the additional values such as CO_2 reduction or energy safety. Another is the requirement of the electrolysis. The most expensive part next to the hydrogen tank is electrolysis modules. The hydrogen productivity, efficiency and cost themselves have a large potential for the development. The performance and longtime stability under the unsteady operation is another essential factor to balance the energy supply and the demand.

In the second topic, to apply the kinetics model of SOFC into the SOEC reaction, the way to extrapolate the rate of EC from that of FC reaction is investigated. Generally, fuel cells have been used with a steady operation with an optimum and/or mild condition and the electrolysis systems have also been used at optimum conditions. On the other hand, to use them in the variable electricity supply and demand, both the input and output power varies (almost randomly), so to operate in unsteady condition is necessary. Thus, the comprehensive understanding for the effect of the unsteady operation to the device performance and the stability are required. The requirement for EC rapidly increases as described in the first topic, but the number of the publications related to the performance of EC is less than 1/20 of FC and the simple reaction kinetics of SOEC is not sufficiently developed. In our present study, several times higher hydrogen generation rate by SOEC was observed compared to the expected value calculated from the SOFC kinetics model. To reinvestigate the chemical and electrochemical equilibrium on TPB is required and the scientific basis of the catalysis and surface inorganic chemistry helped to discuss the difference of the mechanisms between SOFC and SOEC.

Conclusions and Perspectives

Under the common target as utilizing the hydrogen energy storage in the distributed grid, we focused on two different topics: one is to evaluate the feasibility of the storage system by using the 1-min resolution real data stored in "ENE-Swallow" and another is to establish the kinetics model of SOEC from the background of SOFC. In general, these two research topics are carried out by totally different research field and those have separately developed. On the other hand, to apply the energy related technology in the future society, to develop the common scenario based on both of the point of view as the elemental technology and the total system is necessary. In order to apply a technology into the society, to understand how the materials and devices are operated in the real system and what is the real "key issue" to establish the system is important. On the other hand, to develop the management system, to know the performance of the devices under the real and unsteady condition and the limits is necessary. In other words, many positive feedbacks to each other were given by study the both topics in parallel. Our next step is to develop the energy management system which is already applied on Tokyo Tech. By establishing the way to forecast the electricity demand and unsteady supply from VRE based on the "energy big data" stored in "ENE-Swallow" and by installing the storage devices and/or systems with a best mix based on the scientific basis, a distributed grid cooperating with the central grid will be established.

Acknowledgements

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Kei HASEGAWA

長谷川 馨

Assistant Professor
Department of Chemical Science and Engineering
School of Materials and Chemical Technology
Tokyo Institute of Technology
Ph. D.