

Mass Transport and Discharging Dynamics of Redox Flow Battery for Power Supply

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Mass Transport and Discharging Dynamics of Redox Flow Battery for Power Supply

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Abstract

Batteries are essential for the future of power grid. A number of renewable energy sources are being added to the power grid. Energy production with renewable energy sources includes the variation in several times scales. The variation brings in the difficulty of grid balancing. Batteries have quick response and large capacity, and these features enable the batteries to absorb the variations in the power grid. The use of batteries is expected to solve the challenges due to the installation of renewable energy sources.

Mass transport in batteries is one of the critical factors for power supply with the batteries. The slow rate of mass transport can restrict the power supply. Researchers have tried to make mass transport faster. The approaches have been limited to cell design because mass transport in most of the batteries can not be accelerated from outside of them.

A redox flow battery (RFB) is a secondary battery equipped with the circulation system of the electrolytes, and the electrolyte flow can be controlled by pumping. This battery consists of the output/input part called “cell” and the storage part called “tank.” The electrolytes circulate between the cells and the tanks. The redox reaction consumes the reactants in the cells and converts chemical energy to electrical energy. The supply of the reactants to the cells can also restrict the power supply with RFBs. Controlling the electrolyte flow has the potential to prevent the restriction by mass transport and to maintain the power supply with RFBs.

This dissertation studies the charging/discharging dynamics of the cell and gives direction to the design of the flow control system. For simulating charging/discharging behaviors, the model is introduced based on chemical kinetics and mass transport. Moreover, an indicator is introduced for extracting the restriction by mass transport.

First, the assumptions are put on the redox reactions and the mass transport in

RFBs, and the fundamental equations are introduced for modeling. The fundamental equations are derived from Nernst equation, Butler-Volmer equation, and mass balance equation. Nernst equation and Butler-Volmer equation give the voltage of each cell. Mass balance equation represents the change in the reactant concentration, which governs the charging/discharging dynamics. The assumptions and the fundamental equations become the basis for the modeling and the analysis in this dissertation.

Second, discharging behavior due to the dynamic change in the load current is simulated and analyzed. The simulation focuses on the effect of the flow rate of the electrolytes. The RFB in this simulation is assumed to be so small that the transport time from the tanks to the cells is negligible. The dynamics underlying the discharging behaviors are also analyzed with a dimensionless model for verifying the simulation results.

Third, the model with transport delay is introduced for applying the analysis and the discussion to large RFB systems. The transport time appears as a delay in the charging/discharging dynamics in large RFB systems. The model with transport delay is introduced from the mass balance equation, including the transport time. The charging/discharging dynamics are described by the delay differential equation with the single delay. The validity of this model is examined in the experiment using a proto-type RFB.

Fourth, the method for predicting the current-restriction by mass transport is proposed. In the proposed method, the model with transport delay is applied for simulating the current. In addition to the model, the limited-current is introduced as an indicator for extracting the current-restriction by mass transport. The current-restriction is predicted by comparing the limited-current to the current in the simulation. The proposed method is applied to confirm that the current of the proto-type RFB is restricted by mass transport under the load variation. It is verified that the current is restricted by mass transport in the experiment, as predicted in the simulation.

Finally, the studies mentioned above are summarized, and the future directions for constructing the flow control system are denoted based on the model and the indicator given in this dissertation. The application of RFBs can be enlarged by integrating the additional cell stacks to the circulation system of the electrolytes. The direction for designing the multiple cell stack system is also explained.

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Abbreviations and symbols

Abbreviations

Abbreviation	Meaning
RFB	Redox flow battery
FC	Fuel cell
EMF	Electromotive force
SOC	State of charge
ODE	Ordinary differential equation
DDE	Delay differential equation

Symbols

Symbol	Meaning	Unit
c	Reactant concentration	molL^{-1}
I	Discharging current	A
$E_e(=g(c))$	EMF	V
V	Output voltage of each cell	V
N	Molar amount of reactant in RFB	mol
W	Flow rate of electrolyte in each cell	Lmin^{-1}
τ_d	Transport delay (Transport time)	s

α_c	Volume of electrolyte in each half cell	L
α_t	Volume of electrolyte in each tank	L
T	Temperature	K
r_{rfb}	Internal resistance of each cell	$\text{m}\Omega$
η_i ($i = +$ or $-$)	Overpotential in negative or positive half cell	V
c_{max}	Maximum of c	molL^{-1}
E_{eo}	Standard potential of redox reaction	V
E_{eh}^0	EMF at $c = c_{\text{max}}/2$	V
F	Faraday constant	Cmol^{-1}
R	Gas constant	$\text{Jkg}^{-1}\text{K}^{-1}$
V_{main}	Total voltage of main cells	V
V_{monitor}	Voltage of monitor cell	V
c_{main}	Reactant concentration in each main cell	molL^{-1}
c_{monitor}	Reactant concentration in monitor cell	molL^{-1}
ΔV	Difference between averaged V_{main} and V_{monitor}	V
Δc	Difference between c_{main} and c_{monitor}	molL^{-1}

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Chapter 1

Introduction

Energy storage systems are indispensable components in today's electrical network. The electrical network in the vehicle, the robot, and the power grid is composed of various sources and loads. Renewable energy sources are being integrated into these systems. The power supply with renewable energy sources does not necessarily match the power demand of the loads. Energy storage systems can bridge the gap. Especially, batteries are widely used in several kinds of electrical systems as an energy storage system.

Batteries have the aspect as an electrochemical reactor [1] in addition to the aspect as a component of the electrical network. On the scale of nanosecond or millisecond, the batteries can be idealized as a constant voltage source or a nonlinear capacitors. There is no consideration for the phenomena inside of the batteries. The energy conversion process in the batteries is supported by oxidation-reduction (redox) reaction and mass transport. These phenomena affect the electrical behavior of the batteries on the scale of seconds. The development of batteries as an energy storage system require the knowledge of chemical kinetics and mass transport.

Especially, mass transport is one of the factors which restrict the power supply with batteries. The reactants in the neighborhood of the electrode are consumed by the redox reaction. Mass transport phenomenon, including diffusion, carries the reactants to the electrode. The reactants are depleted when the reactants are supplied slowly. The current is restricted to the rate of mass transport, and the voltage drops. The batteries cannot supply the required power. Most of the batteries do not have any equipment for accelerating mass transport. But, there exist some exceptions: Redox flow batteries (RFBs) [2] and fuel cell (FCs) [3].

The reaction in them is categorized into the flow process [1], and electrolytes are controlled by pumping.

This dissertation aims to give directions for designing the control system of the electrolyte flow, which enables RFBs to avoid the restriction by mass transport. The rest of this chapter is devoted to reviewing the detailed background of this research. Section 1.1 reviews the role and the development of the energy storage systems in the power grid. Section 1.2 explains the development of the RFB systems and the challenges for designing the flow control system.

1.1 Batteries as energy storage system in power grid

1.1.1 Role of energy storage systems

Energy storage systems have been becoming essential elements for the power grid. The energy production is required to reduce CO₂ emission, reliance on imported resources, and cost. These social requests have encouraged the installation of renewable energy sources like wind power and solar power [4, 5]. The energy production with renewable energy sources depends on climate change and varies in several time scales [6]. The time scale ranges from second to hour. The variation is difficult to predict and makes grid balancing difficult. The imbalance between the power supply and the power demand leads to the instability of the frequency and causes serious faults on the power grid. Energy storage systems are expected to solve the imbalance by absorbing the variations.

A variety of energy storage systems have been developed [7]: pumped hydro-electric storages (PHS), compressed air storages (CAES), supercapacitors, superconducting magnetic energy storages (SMES), and batteries. The properties of these energy storage systems are listed in Table 1.1 [8, 9].

Supercapacitors and SMES are classified into electrical energy storage. Supercapacitors store electrical energy in the electrostatic field, and the SMES stores the electrical energy in the magnetic field. Electrical energy storage has quick response and low energy capacity.

The other energy storage systems require the process of energy conversion. PHS stores the electrical energy by converting it to gravitational potential energy of the

Table 1.1: Properties of energy storage systems [8,9].

Energy storage system	Energy capacity	Response time
Supercapacitors	0.0005 MWh	milliseconds
SMES	0.015 MWh	milliseconds
PHS	180 – 8000 MWh	minutes
CAES	0.002 – 2860 MWh	minutes
Batteries	0.0005 – 244.8 MWh	milliseconds

water, and CAES converts electrical energy to potential energy of the compressed air. These energy storage systems are classified into mechanical storage. Mechanical storage can store large energy but respond to the load variation slowly.

Batteries are classified into chemical energy storage. They convert the electrical energy into chemical energy through the redox reaction. Batteries have both large energy capacity and quick response.

Energy storage systems provide several kinds of services to the power grid. These services can be classified into two groups concerning the time scale [10]. One is the long-time operation, including load-balancing and peak-shaving [11, 12]. For these services, energy storage systems absorb or release the electrical power on an hourly scale according to the power demand. The large energy capacity is needed for the long time operation. The other is the short-time operation and includes regulation of frequency and maintaining power quality [13, 14]. For the short-time operation, the energy storage systems should respond to the disturbances in the load power in milliseconds or seconds.

The long-time operation and the short-time operation require different features, and suitable energy storage systems should be chosen for the services. Considering the properties in Table 1.1, PHS and CAES are suitable for the long-time operation due to the large energy capacity. The quick response of supercapacitors and SMES are used for the short-time operation. Batteries have large energy capacity and quick response. They can be applied to both the long-time operation and the short-time operation.

1.1.2 Development of batteries focusing on mass transport

The use of batteries as an energy storage system in the power grid dates back to the 1880s [15]. A lead-acid battery was installed on the power grid for load-leveling. Batteries in the power grid requires the large power capacity and energy capacity. The researchers have made efforts to scaling-up these properties while looking for other candidates [16]. Today, lead-acid batteries, Li-ion batteries [17,18], sodium-sulfur batteries [19,20], nickel-cadmium batteries [21,22], and RFBs are gathering attention as energy storage systems for the power grid.

Some trials for scaling up the batteries focused on the transport of the reactants inside of them. As mentioned above, the transport of the reactants inside of the batteries can restrict the current. Especially, it is reported that the power supply at a high rate is restricted by the diffusion inside of batteries [23,24]. The diffusion of the reactants in the lead-acid battery was improved by decreasing the thickness of the electrode [25,26]. A similar approach was taken for increasing the output current of the Li-ion battery [24]. The transport systems have been improved by cell design.

RFBs are equipped with the pumping system, which can accelerate the electrolyte flow. The flow control system has the potential to enable RFBs to supply power without the restriction by mass transport. Controlling mass transport is becoming an issue in battery management systems [27].

1.2 Redox flow battery

1.2.1 Overview of development

The schematic diagram of an RFB is shown in Figure 1.1. This battery consists of cells and tanks. A redox reaction occurs in the cells. This reaction converts chemical energy to electrical energy, and vice versa. The series-connected cells determine the output power. The negative and positive electrolytes are separately stored in the tanks. The energy capacity is determined by the volume of the tanks. The electrolytes circulate between the cells and the tanks due to the pumping.

An old research of the RFB with the structure in Figure 1.1 can be found in the patent [28], which was written by a researcher at NASA. NASA's RFB system was developed as an extension of FCs, and employed iron/chromium as the positive and

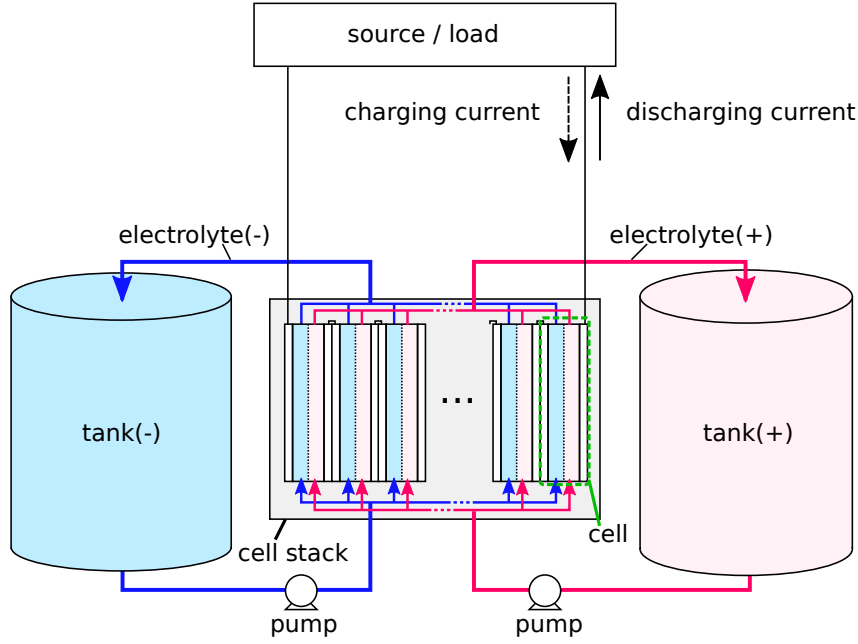


Figure 1.1: Schematic diagram of redox flow battery.

negative electrolytes. The iron/chromium has the advantages of low cost and high availability. However, the energy density and the electromotive force (EMF) is low. A number of the redox couples have been explored for scaling-up the power and energy capacity of RFBs [29–31]. Iron/chromium RFBs, polysulfide/bromine RFBs, and all-vanadium RFBs are known to achieve the fielding test and commercialization [30, 31]. The properties of these redox flow batteries are listed in Table 1.2.

The problem of capacity decay [32] has also been concerned with the selection of the redox couple. A cell is divided into the positive and negative half cells by the membrane. The membrane cannot completely separate the positive and negative electrolytes. The ions go across the membranes, and the capacity decreases due to the cross-contamination of the electrolytes. All-vanadium RFBs [2] can solve this problem. The capacity decay due to the cross-contamination can be recovered by mixing the negative and positive electrolytes and charging the cells again [31–33]. All-vanadium RFBs are the majority of the commercialized RFBs due to this advantage. Hereafter, the term RFB refers to all-vanadium RFB.

In Japan, the development of the RFBs began in 1986 [34]. More than 20 systems have already been installed, including the demonstration systems [35–38]. These RFB systems have provided a variety of services. A 450 kW RFB system was

Table 1.2: Properties of redox couples [31,32]

Redox couple	Standard potential	Energy density
Iron/Chromium	1.18 V	$< 10 \text{ Whkg}^{-1}$
Polysulfide/Bromine	1.36 V	$65 - 75 \text{ Whkg}^{-1}$
All-Vanadium	1.25 V	$25 - 30 \text{ Whkg}^{-1}$

erected in the Tatsumi Substation of the Kansai Electric Power Co., Ltd and worked for load-leveling in 1996 [36]. An RFB was also developed for compensating voltage sag [39] and installed into a semiconductor plant in 2001 [37]. In the same year, A MW class RFB had begun to provide the services of load-leveling and smoothing output power of the wind farm in Tomamae Winvilla power plant of Electric Power Development Co., Ltd [38].

1.2.2 Challenges for designing flow control system

The reactant concentration in the cells is one of the dominant state variables in the management of the RFBs. The state of charge (SOC) is defined by the concentration of the reactants for discharging reaction [40]. The EMF is also determined by these reactants, as Figure 1.2 shows. The depletion of them corresponds to the over-discharge, and the saturation corresponds to the over-charge.

Over-charge and over-discharge cause problems in the use of RFB. A gassing side reaction occurs in the over-charged cells [41,42]. The gasses produced by the side reaction disturbs the electron transfer from the electrode and damages the cells. The over-discharge of the cells does not cause such a side reaction, but a serious problem occurs in the power supply. The voltage drops, and the current is restricted by mass transport. The power converters cannot arbitrarily withdraw the power from the over-discharged cells.

The charging/discharging dynamics of the cells are governed by two parameters: current and flow rate of electrolytes. The redox reaction consumes the reactants in the cells, and the rate of the redox reaction is proportional to the current. The mass transport from the tanks to the cells supplies the reactants to the cells. The flow rate of the electrolytes determines the rate of mass transport.

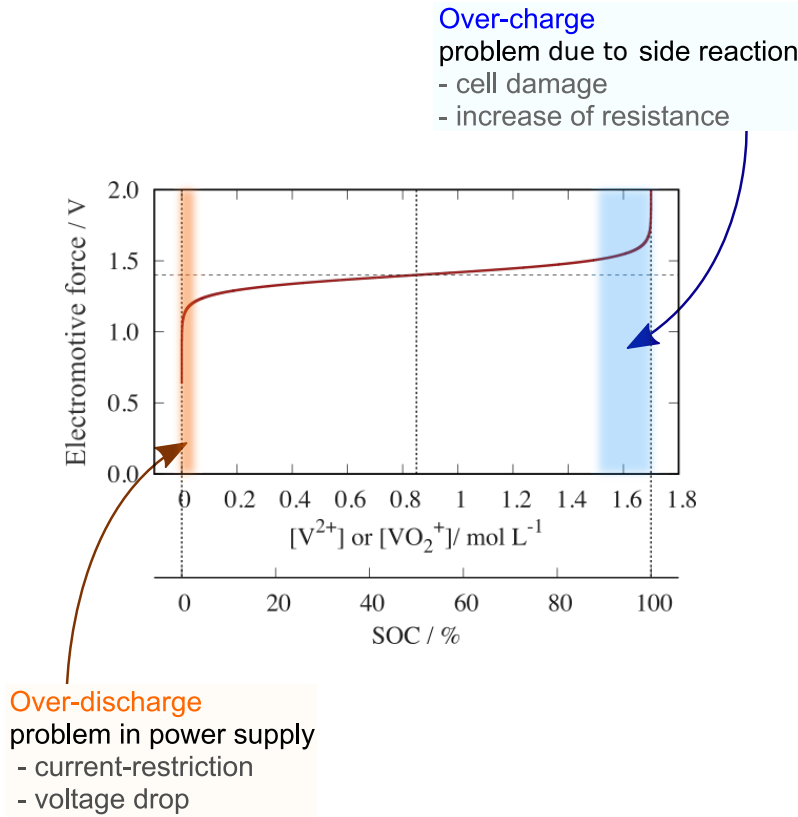


Figure 1.2: Dependence of EMF and SOC on concentration of reactants for discharging reaction.

Controlling the current and the flow rate of the electrolytes is critical for maintaining the power supply with RFBs. The sudden increase of the current accelerates the consumption of the reactants in the cells. The slow rate of mass transport leads to over-discharging of the cells even if a lot of reactants remain in the tanks. The voltage changes nonlinearly with the reactant concentration, and it is difficult to predict the over-discharge only by monitoring the voltage. The current and the flow rate of the electrolytes should be controlled based on the prediction for avoiding over-discharge and the restriction in the power supply.

The control systems before the 2010s set the limitation on the SOC and control the current within the limitation [43,44]. The flow rate of the electrolytes is fixed in these control systems. The limitation prevents the over-charge and over-discharge of the cells. The power withdrawn from an RFB is also suppressed due to the limitation on the SOC even though the RFB can increase the output power by pumping up

the electrolyte flow.

In the past decade, the flow control system has begun to gather researchers' attention. The flow control systems [45–49] aim to minimize the loss derived from the pumping and the concentration overpotential¹ [50]. The concentration overpotential appears according to the heterogeneity in the distribution of the reactants inside of the cells. The heterogeneity is solved by the fast rate of the electrolyte flow. The flow control systems can optimize the system efficiency within the limitation on the SOC.

The validity of the limitation should be discussed for supplying the requested power to the load. The upper limit is critical for preventing the gassing side reaction, and the chemical researchers have investigated the condition for occurring the gassing side-reaction and its effect [41,42]. On the other hand, discharging behavior has not been investigated for the low concentration of reactants. There is no rationale for the lower limit on the SOC. The condition for the restriction by mass transport is expected to depend on the flow rate of the electrolytes and the current. A reasonable indicator should be established for extracting the over-discharge and the restriction of the power supply by mass transport. If discharging dynamics for the low concentration of reactants are clarified, the understanding of the dynamics will help to find out the indicator.

A suitable model should be chosen for simulating and analyzing discharging behavior. Along with the transition in the control systems, various models have been developed [51]. The control systems of the current [43,44] are based on the equivalent circuits [52,53] and estimates the change of SOC with coulomb counting method² [54]. The estimation neglect the mass transport from the tanks to the cells. The flow control systems [45,47,49] employ the models [55–57], which have been introduced based on chemical kinetics and mass transport. The models include the flow rate of the electrolytes as the parameter, and reflects it in the simulation.

The transport time also characterizes the mass transport from the tanks to the cells, but the previous models [55–57] neglect it. The dynamics in mass transport is slow with the comparison to the dynamics in the electrical circuit. The transport time is expected to appear as a delay in charging/discharging dynamics, especially in the large RFB systems. The model considering the delay derived from the transport

¹Concentration overpotential is also called “diffusion overpotential” or “concentration polarization”.

²Coulomb counting method is also called “ampere-hour counting method”.

time (transport delay) also should be constructed for simulating the discharging behavior affected by mass transport.

1.3 Overview of dissertation

This dissertation addresses the relationship between mass transport and the discharging behavior of the cells. The models of charging/discharging dynamics are introduced with consideration for the mass transport from the tanks to the cells. The discharging behavior is studied with the models and a proto-type RFB. The direction for controlling the electrolyte flow is given from the understanding of the dynamics governing the discharging behavior.

Chapter 2 explains the assumptions and the fundamental equations for the modeling. Redox reactions and mass transport in RFBs are complicated, and the assumptions are needed for simplifying the phenomena. Based on the assumptions, the fundamental equations are introduced from Nernst equation [58], Butler-Volmer equation [58], and mass balance equation [59]. Nernst equation and Butler-Volmer equation associate the charging/discharging behavior of the cells to the electrical behavior of the RFB. Mass balance equation becomes the basis for describing the charging/discharging dynamics with differential equations.

Chapter 3 simulates and analyzes the discharging behavior due to the dynamic change in the load current. The simulation focuses on the effect of the flow rate of the electrolytes. The RFB is assumed to be so small that the transport time from the tanks to the cells is negligible. The simulation applies the model for micro RFB [55], which is introduced from the mass balance equations in Chapter 2 by neglecting the transport time. Moreover, the dynamics governing the discharging behavior are also analyzed with a dimensionless state equation for verifying the simulation results.

Chapter 4 develops the model with transport delay for extending the discussion to the large RFB systems. The proto-type RFB is employed for the experiment, in which the effect of the delay derived from the circulation system is observed. The model with transport delay is introduced for simulating the charging/discharging behavior of the proto-type RFB. The introduction process is based on the mass balance equations in Chapter 2. The validity of the model is examined by comparing the simulation results with the experimental results.

Chapter 5 proposes the method for predicting the current-restriction by the mass transport from the tanks to the cells, the occurrence of which is indicated by the numerical study in Chapter 3. The model with transport delay in Chapter 4 is used to simulate the discharging current. In addition to the model, the “limited-current” is introduced for extracting the current-restriction. The limited-current is calculated from the rate of the mass transport. The current-restriction is predicted by comparing the simulated current to the limited-current. The proposed method is applied for predicting the current-restriction of the proto-type RFB under the load variation. The prediction is verified with the proto-type RFB in the experiment.

Chapter 6 summarizes the studies in this dissertation and shows the direction for designing the flow control system. The current-restriction by the mass transport from the tanks to the cells can be avoided by controlling the electrolyte flow based on the prediction. The more detailed idea and the remained challenges are also explained. Moreover, the possibility of enlarging the application of RFBs is also suggested.

Chapter 2

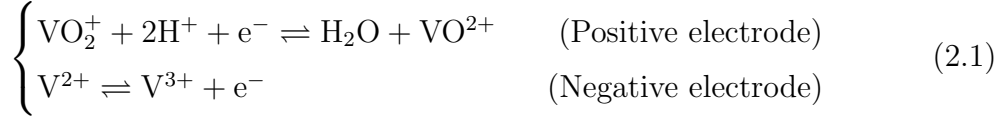
Assumptions and fundamental equations for modeling

This chapter puts the assumptions on the phenomena in RFBs and introduces the fundamental equations for modeling. Redox reactions and mass transport in RFBs are complicated, and it is difficult to consider all of the phenomena in the modeling process. The modeling researches [51, 55, 57, 60] put the assumptions according to their purpose. These models are developed from the fundamental equations, which are introduced based on the assumptions. The fundamental equations are introduced from Nernst equation [58], Butler-Volmer equation [58], and mass balance equation [59]. Nernst equation and Butler-Volmer equation give the voltage of the cell. Mass balance equation becomes the basis for introducing the differential equation of the reactant concentration. This chapter puts the assumptions for focusing on the effect of the mass transport from the tanks to the cells. Section 2.1 explains the phenomena governing the charging/discharging of the cells and lists up the assumptions. Section 2.2 introduces the fundamental equations based on the assumptions. Section 2.3 shows the process for developing the model of micro RFB [55] from the fundamental equations as an example.

2.1 Assumptions on phenomena in RFB

2.1.1 Redox reactions and mass transport in RFB

This subsection explains redox reactions and mass transport governing the charging/discharging process. Following redox reaction (2.1) occurs in the cell connected to a load or a source, as Figure 2.1 shows.



Redox reaction (2.1) accompanies with the transfer of H^+ between the negative and positive half cells.



The forward and reverse reactions correspond to discharging and charging reactions, respectively. V^{2+} , VO_2^+ , and H^+ are the reactants for the discharging reaction, and V^{3+} and VO^{2+} are the reactants for the charging reaction. The cell keeps discharging or charging as long as these reactants are supplied from the tanks.

In addition to redox reaction (2.1), the side reactions [41, 61] are known to affect the charging/discharging behavior. One of the well-known side reactions is caused by the cross-contamination of the electrolytes. The membrane cannot completely prevent the cross-contamination. V^{2+} and V^{3+} move to the positive half cell, and VO^{2+} and VO_2^+ move to the negative half cell. These ions cause the self-discharge reactions leading to the capacity loss. Another side reaction is the gassing reaction, which produces hydrogen and oxygen gas. The internal resistance increases due to the hydrogen and oxygen gas.

The mass transport in the RFB can be divided into two types: the transport via the pipes and the diffusion inside of the cell. The former supplies the reactants from the tanks to the cells. The later carries the reactants in the bulk to the electrodes. The rate of diffusion is affected by the flow rate of the electrolytes, and it is difficult to evaluate the diffusion and transport via the pipes separately.

2.1.2 Assumptions

The following assumptions are put on the redox reactions and the mass transport.

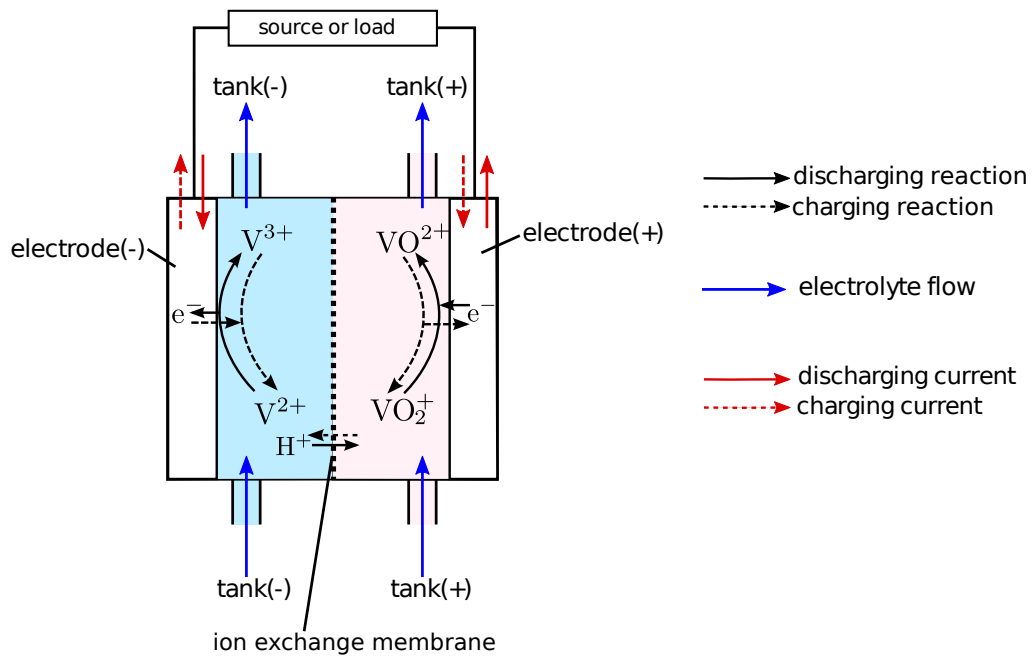


Figure 2.1: Charging/discharging process in cell. The redox reaction consumes the reactants in the cell and converts energy. H^+ transfers via the ion exchange membrane. The reactants are supplied to the cell due to the circulation system of the electrolytes.

- (a1) The concentration gradient of the reactants between the bulk and the electrode is negligible.
- (a2) The reactants in the tanks are instantly mixed.
- (a3) The ions cannot go across the membrane except for H^+ .
- (a4) The negative and positive sides keep symmetry in the rate of redox reaction (2.1) and the rate of mass transport.
- (a5) The variation in the amount of H^+ does not affect the EMF.
- (a6) The reactants in the tanks require the transport time τ_d to reach the cells.

The previous research [55] also puts the same assumptions as assumptions (a1)–(a5). Assumption (a6) is added for considering the transport time between the tanks and the cells.

Assumptions (a1)–(a4) allow simplifying the distribution of the reactants. For the fast rate of the electrolyte flow, assumptions (a1) and (a2) are satisfied, and the distribution of the reactants can be uniformed in the cells and the tanks. The capacity decay due to the cross-contamination critically appears after 100 cycles [62]. The cross-contamination of vanadium ions is negligible in one charging/discharging cycle, as written in assumption (a3). The charging/discharging processes in the negative and positive half cells keep symmetry due to assumptions (a3) and (a4). The symmetry between the negative and positive half cells restricts the reactant concentration as equation (2.3) and reduces the number of variables.

$$[V^{2+}] = [VO_2^+] = c, \quad [V^{3+}] = [VO^{2+}] = c_{\max} - c \quad (2.3)$$

$c_{\max}$ is the maximum of the concentration of the vanadium ions, which are solved in the negative and positive electrolytes. $c \in (0, c_{\max})$ is defined as the reactant concentration. The modeling process does not need to consider both the phenomena in the negative side and the positive side due to the symmetry.

The charging/discharging of a cell is also defined as the increase/decrease of the reactant concentration in the cell, and the SOC is given as equation (2.4) [40].

$$SOC = \frac{[V^{2+}]}{[V^{3+}] + [V^{2+}]} = \frac{[VO^{2+}]}{[VO^{2+}] + [VO_2^+]} = \frac{c}{c_{\max}} \quad (2.4)$$

The variation in the amount of H^+ can be neglected due to assumption (a5). Assumption (a5) has already been verified in the experiment [63].

2.2 Fundamental equations

Suppose that an RFB consists of the series-connected cells and one couple of the tanks. The fundamental equations are introduced for modeling this RFB.

2.2.1 EMF from Nernst equations

The EMF of the cell is given by Nernst equation [58].

$$E_e = E_{eo} + \frac{RT}{F} \ln \frac{[V^{2+}][VO_2^+][H^+]}{[V^{3+}][VO^{2+}]} \quad (2.5)$$

Here, E_{eo} is the standard potential of redox reaction (2.1). R is gas constant, and T is the temperature. F is Faraday constant. Nernst equation is simplified due to restriction (2.3).

$$E_e = E_{eo} + \frac{RT}{F} \ln[H^+] + \frac{2RT}{F} \ln \frac{c}{c_{\max} - c} \quad (2.6)$$

Assumption (a5) allows treating the second term as constant. The EMF of the cell is given by nonlinear function, $g(c)$.

$$E_e = E_{eh}^0 + \frac{2RT}{F} \ln \frac{c}{c_{\max} - c} = g(c) \quad (2.7)$$

Here, $E_{eh}^0 = E_{eo} + RT/F \ln[H^+]$ is the EMF at $c = c_{\max}/2$. In equation (2.7), the EMF monotonically increases with the reactant concentration c and SOC.

2.2.2 Output voltage from Butler-Volmer equation

The output voltage of each cell is given by the following equation when the cell is connected to a load or a source.

$$V = E_e - RI - (\eta_- + \eta_+) \quad (2.8)$$

R is the ohmic resistance of the electrodes. η_+ and η_- are called overpotential [58] in the negative and positive half cells. The overpotential represents the loss derived from redox reaction (2.1).

Butler-Volmer equation [58] gives the relationship between the discharging current and the overpotential in the negative half cell.

$$\frac{I}{A} = i_{o-} \left\{ \frac{c_2^s}{c_2^b} \exp\left(\frac{-\alpha_- F}{RT} \eta_- \right) - \frac{c_3^s}{c_3^b} \exp\left(\frac{(1 - \alpha_-) F}{RT} \eta_- \right) \right\} \quad (2.9)$$

Butler-Volmer equation is derived from the rate of redox reaction (2.1). A is the area of the negative electrode. The first and second terms in equation (2.9) correspond to the rate of forward and reverse reaction in the negative half cell, respectively. The variables c_2^k and c_3^k ($k = s, b$) represent the concentration of V^{2+} and V^{3+} . The superscript k indicates that the variable refers to the concentration in the surface of the electrode ($k = s$) and in the bulk ($k = b$). i_{o-} is the exchange current density, and $\alpha \in (0, 1)$ is called the charge-transfer coefficient. i_{o-} and α_- are constant for fixed electrode potential.

Assumption (a1) implies that $c_l^s/c_l^b = 1$ ($l = 2, 3$). Suppose that $\eta_- \ll \alpha_- F/RT$ and $\eta_- \ll (1 - \alpha_-)F/RT$. The Butler-Volmer equation (2.9) is linearized around $\eta_- = 0$.

$$I = \frac{1}{r_-} \eta_- \quad (2.10)$$

r_- is the resistance derived from the overpotential in the negative half cell.

$$r_- = \frac{RT}{F i_{o-} A} \quad (2.11)$$

The same process can be applied to introduce the resistance derived from the overpotential in the positive half cell, r_+ .

The output voltage of each cell is simplified with r_+ and r_- as equation (2.12).

$$\begin{aligned} V &\approx E_e - RI - (r_- I + r_+ I) \\ &= E_e - r_{\text{rfb}} I \end{aligned} \quad (2.12)$$

Here, $r_{\text{rfb}} (= R + r_- + r_+)$ is referred as the internal resistance.

2.2.3 Mass balance equation

Figure 2.2 describes the mass balance of reactant (V^{2+} or VO_2^+) in each half cell and the RFB. m is the number of the cells. The cross-contamination of vanadium ions via the membrane is neglected due to assumption (a3). The mass balance equations of the reactant are introduced here.

$$\frac{d(\alpha_c c(t))}{dt} = -\frac{I(t)}{F} + W(c_{\text{out}}(t) - c_{\text{in}}(t)) \quad (2.13)$$

$$\frac{dN(t)}{dt} = -\frac{mI(t)}{F} \quad (2.14)$$

Here, the first terms in mass balance equations (2.13) and (2.14) are corresponding to the consumption rate, which is given by Faraday's law [64]. $I(t)$ is the discharging current, and α_c is the volume of electrolyte in each half cell. $W_{c_{in}}(t)$ and $W_{c_{out}}(t)$ represent the flowing in/out of the reactant. W is the flow rate of the electrolyte, which has the unit of $Lmin^{-1}$. $N(t)$ is the molar amount of the reactant in the RFB.

$$N(t) = m\alpha_c c(t) + c_{\text{tank}}(t) \quad (2.15)$$

The reactant concentration in the tank is also uniformed as c_{tank} due to assumption (a2).

Assumption (a1) secures that flowing out of the reactant is determined by the reactant concentration in the cell. Assumption (a6) says that the reactant flowing in the cell at $t = t$ distributes in the tank at $t = t - \tau_d$. Here mass balance equation in the cell (2.13) is rewritten as equation (2.16).

$$\frac{dc(t)}{dt} = -\frac{I(t)}{\alpha_c F} + \frac{W}{\alpha_c} (c_{\text{tank}}(t - \tau_d) - c(t)) \quad (2.16)$$

2.3 Introduction of model for micro RFB

This subsection shows the introduction process of the model for micro RFB [55] as an example. The transport system in the micro RFB is small, and the transport time, τ_d , is negligible.

Mass balance equations in the cell and the micro RFB are given by rewriting equations (2.14)–(2.16).

$$\frac{dc(t)}{dt} = -\frac{I(t)}{F} + \frac{W}{\alpha_c} (c_{\text{tank}}(t) - c(t)) \quad (2.17)$$

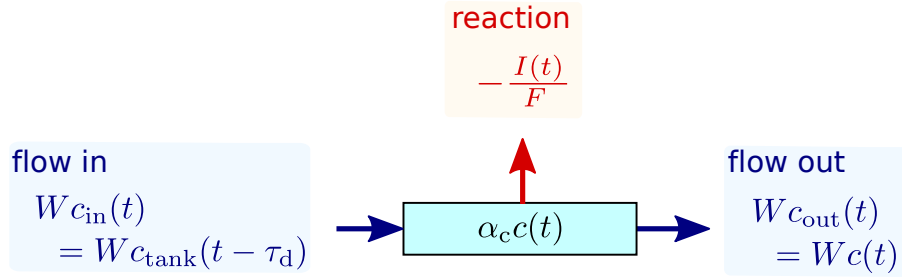
$$\frac{dN(t)}{dt} = -\frac{I(t)}{F} \quad (2.18)$$

$$N(t) = \alpha_c c(t) + \alpha_t c_{\text{tank}}(t) \quad (2.19)$$

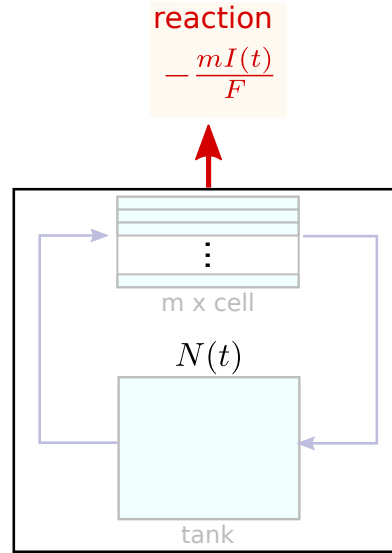
Here, $m = 1$.

Suppose that equations (2.17) and (2.19) are differentiable. The following equation is given by differentiating mass balance equation (2.17).

$$\frac{d^2 c(t)}{dt^2} = -\frac{1}{\alpha_c F} \frac{dI(t)}{dt} + \frac{W}{\alpha_c} \left(\frac{dc_{\text{tank}}(t)}{dt} - \frac{dc(t)}{dt} \right) \quad (2.20)$$



(a) Mass balance in each half cell.



(b) Mass balance in RFB.

Figure 2.2: Mass balance of reactant (V^{2+} or VO_2^+) in each half cell and RFB. The RFB consists of series connected cells and one couple of the tanks. m is the number of the cells. I is the discharging current. W is the flow rate of the electrolytes. $c(t)$ and $c_i(t)$ ($i = \text{in, out, tank}$) refer to the reactant concentration. $N(t)$ is the molar amount of reactant in the RFB. α_c refers to the volume of electrolyte in each half cell.

$dc_{\text{tank}}(t)/dt$ is given by differentiating equation (2.19) and substituting it into mass balance equation (2.18).

$$\begin{aligned}\frac{dN(t)}{dt} &= \alpha_c \frac{dc(t)}{dt} + \alpha_t \frac{dc_{\text{tank}}(t)}{dt} \\ \frac{dc_{\text{tank}}(t)}{dt} &= -\frac{I(t)}{\alpha_t F} - \frac{\alpha_c}{\alpha_t} \frac{dc(t)}{dt}\end{aligned}\quad (2.21)$$

The time evolution of the reactant concentration in the cells is given by substituting the $dc_{\text{tank}}(t)/dt$ into equation (2.20).

$$\frac{d^2c(t)}{dt^2} = -W \left(\frac{1}{\alpha_c} + \frac{1}{\alpha_t} \right) \frac{dc(t)}{dt} - \frac{WI(t)}{\alpha_c \alpha_t F} - \frac{1}{\alpha_c F} \frac{dI(t)}{dt} \quad (2.22)$$

2.4 Summary

This chapter listed up the assumptions on the phenomena and introduced the fundamental equations for modeling. The voltage of the cell was given by the simplified Nernst equation and Butler-Volmer equation. The dynamics in the reactant concentration were introduced from the mass balance equations, as shown in Section 2.3. These fundamental equations are the basis for the modeling and the analysis in the later chapters. The model for micro RFB is used for simulating discharging behavior in Chapter 3. Chapter 4 develops the model with transport delay from the mass balance equations.

Chapter 3

Discharging dynamics of micro RFB in electrical circuit

This chapter numerically studies the discharging behavior due to the dynamic change of current. The previous researches [57,65] investigated the effect of the flow rate of the electrolyte on the charging/discharging behavior. The researches do not consider the sudden increase of the current, which leads to the rapid consumption of the reactant and over-discharge. The electrolyte flow is critical for avoiding the over-discharge in such case, and its effect should be clarified. This study simulates the discharging behavior of an RFB in the electrical circuit by using the model for micro RFB [55]. This model includes the flow rate of the electrolyte as a parameter and neglects the transport time. Section 3.1 shows the setup and the results of the simulation. Section 3.2 clarifies the dynamics underlying the discharging behavior for verifying the simulation results.

3.1 Simulation of discharging behavior

3.1.1 Simulation setup

This subsection explains the settings and the tools for the simulation. The model for micro RFB has already been introduced in Section 2.3. The discharging behavior of the RFB in the circuit can be simulated by adding the differential equation of current to the model.

Figure 3.1 shows the target system of the simulation. The RFB is integrated

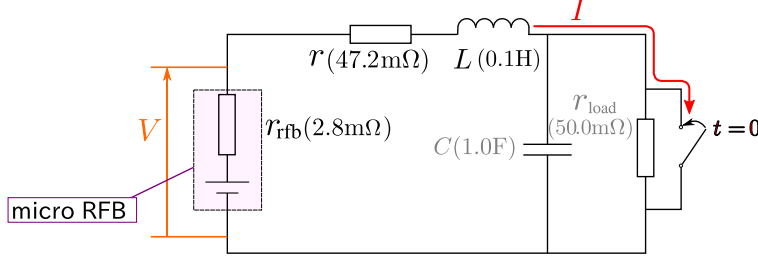


Figure 3.1: Target system of simulation which integrates micro RFB. V is the output voltage of the micro RFB, and r_{rfb} is the internal resistance. The load of the RFB has changed in a step at $t = 0$.

into the electrical circuit. This RFB consists of one cell and one couple of the tanks. At $t = 0$, the switch turns on, and the current changes dynamically due to the short-circuit.

Kirchhoff's voltage law is established as equation (3.1) for $t > 0$.

$$V(t) - L \frac{dI(t)}{dt} - rI(t) = 0 \quad (3.1)$$

V is the output voltage of the cell, which is given by fundamental equations (2.7) and (2.12) in Section 2.2. The ODE of discharging current is given by substituting fundamental equations (2.7) and (2.12) into equation (3.1) as follows.

$$\begin{aligned} \frac{dI(t)}{dt} &= -\frac{1}{L} \{ (r + r_{\text{rfb}})I(t) - g(c(t)) \} \\ &= -\frac{1}{L} \left\{ (r + r_{\text{rfb}})I(t) - \left(E_{\text{eh}}^0 + \frac{2RT}{F} \frac{c(t)}{c_{\text{max}} - c(c)} \right) \right\} \end{aligned} \quad (3.2)$$

r_{rfb} is the internal resistance of the cell, and $g(c)$ gives the EMF. c refers to the reactant concentration in the cell.

Equation (3.3) is given by substituting (3.2) into ODE (2.22).

$$\begin{aligned} \frac{d^2c(t)}{dt^2} &= -W \left(\frac{1}{\alpha_c} + \frac{1}{\alpha_t} \right) \frac{dc(t)}{dt} - \frac{WI(t)}{\alpha_c \alpha_t F} - \frac{1}{\alpha_c F} \frac{dI(t)}{dt} \\ &= -W \left(\frac{1}{\alpha_c} + \frac{1}{\alpha_t} \right) \frac{dc(t)}{dt} + \left(\frac{r + r_{\text{rfb}}}{L} - \frac{W}{\alpha_t} \right) \frac{I(t)}{\alpha_c F} \\ &\quad - \frac{1}{\alpha_c F L} \left(E_{\text{eh}}^0 + \frac{2RT}{F} \ln \frac{c(t)}{c_{\text{max}} - c(t)} \right) \end{aligned} \quad (3.3)$$

Table 3.1: Parameters of RFB and circuit (ref. [55, 66]).

Parameter	Meaning	Value	Unit
α_c	Volume of electrolyte in each half cell	0.1	L
α_t	Volume of electrolyte in each tank	0.9	L
T	Temperature	307	K
$c_{\max}$	Maximum concentration of vanadium ions	1.7	molL ⁻¹
L	Inductance in circuit	0.1	H
C	Capacitance in circuit	1.0	F
r_{rfb}	Internal resistance of cell	2.8	m Ω
r	Resistance in circuit	47.2	m Ω
r_{load}	Load resistance	50.0	m Ω

The discharging behavior can be simulated by solving the ODEs (3.2) and (3.3). The parameters of the RFB are set at the values listed in Table 3.1.

The following initial condition is set for the simulation.

$$\frac{dI(t)}{dt} = 0 \quad (t \rightarrow -0), \quad c(0) = c_{\text{tank}}(0). \quad (3.4)$$

The reactant concentration should be positive, and the finishing condition is given as equation (3.5).

$$c(t) \leq 0 \quad (3.5)$$

In this simulation, the forth-order Runge-Kutta method [67] is adopted to solve the ODEs (3.2) and (3.3). The step size is fixed at $h = 0.001$ s.

3.1.2 Discharging behavior classified into three cases

Figure 3.2 shows the simulation results. The flow rate is set at $W = 0.050$ Lmin⁻¹, 0.100 Lmin⁻¹, and 0.200 Lmin⁻¹. The initial value of the reactant concentration

in the cell is fixed at $c(0) = 0.125 \text{ molL}^{-1}$. Discharging behavior varies depending on the flow rate of the electrolyte. As Figures 3.2(a) and (b) show, for $W = 0.050 \text{ Lmin}^{-1}$, the current and the EMF quickly drop, and the discharging stops at the drops. For $W = 0.100 \text{ Lmin}^{-1}$ and 0.200 Lmin^{-1} , the current and the EMF decrease slowly with comparison to the discharging behavior for $W = 0.050 \text{ Lmin}^{-1}$. When the flow rate is set at $W = 0.100 \text{ Lmin}^{-1}$, the oscillation appears in the current and the voltage. Figure 3.2(c) shows the time evolution of the reactant concentration in the cell. The significant difference of discharging behaviors appears at the low concentration of the reactant in the cell.

The reactant concentration in the tank also characterizes of the discharging behaviors. The hashed line in Figure 3.2(c) describes the time evolution of reactant concentration in the tank, which is given by solving ODE (2.21). For $W = 0.050 \text{ Lmin}^{-1}$, the discharging stops early without consuming the reactant in the tank. The slow rate of mass transport is considered to result in the depletion of the reactant in the cell and the stop of discharging. For $W = 0.100 \text{ Lmin}^{-1}$ and 0.200 Lmin^{-1} , the cell finishes the discharging after the reactant in the tank is consumed. The reactant in the tank is supplied to the cell at sufficient rate.

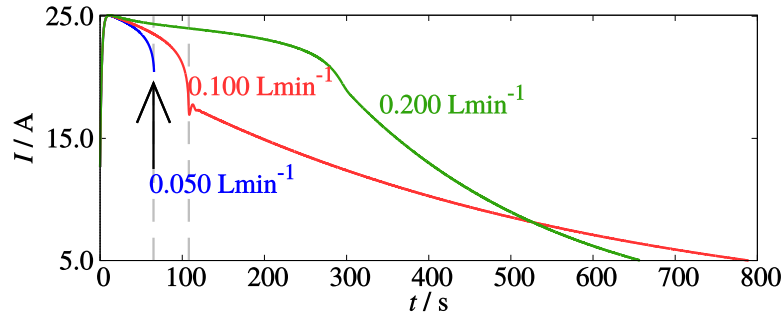
Here, equation (3.6) defines the consumption rate of the reactant in the tank.

$$\varepsilon_t = \frac{c_{\text{tank}}(0) - c_{\text{tank}}(t_f)}{c_{\text{tank}}(0)} \quad (3.6)$$

t_f refers to the time at which the discharging has finished.

The color map in Figure 3.3(a) shows the consumption rate of the reactant in the tank. The horizontal axis refers to the flow rate of the electrolyte, and the vertical axis to the initial value of the reactant concentration in the cell. The consumption rate is calculated for $W = 0.001 \text{ Lmin}^{-1}$ – 0.200 Lmin^{-1} and $c(0) = 0.01 \text{ molL}^{-1}$ – 1.00 molL^{-1} . A boundary appears in the color map and divides this color map into two regions. The reactant in the tank is consumed for the conditions which are located above the boundary. The discharging finishes without consuming the reactant in the tank for the conditions which are located under the boundary.

The discharging behaviors can be classified into three cases, and the color map in Figure 3.3(a) clarifies the condition for these cases. Figure 3.3(b) shows the simulation results under the conditions A1–A4. The conditions A1 and A4 are located above the boundary on the color map, and the conditions A2 and A3 are located under the boundary. For the conditions A2 and A3, the RFB behaves



(a) Current in circuit.

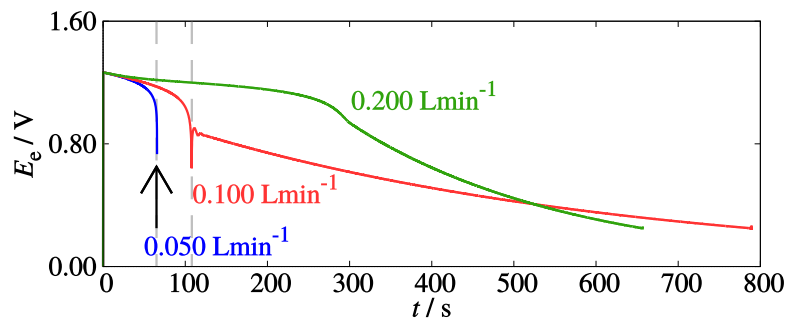
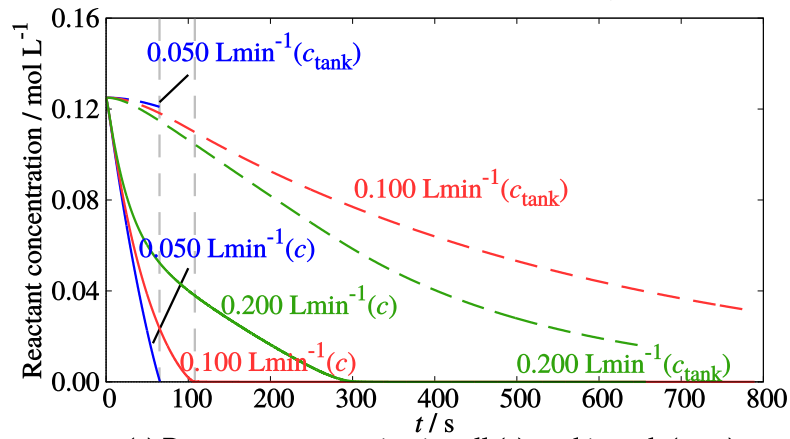
(b) Electromotive force of RFB (E_e).(c) Reactant concentration in cell (c), and in tank (c_{tank}).

Figure 3.2: Simulated discharging behavior of cell for the dynamic current change. The initial value of the reactant concentration in the cell is fixed at 0.125 mol L^{-1} . The flow rate is set at $W = 0.050 \text{ Lmin}^{-1}$, 0.100 Lmin^{-1} , and 0.200 Lmin^{-1} . c and c_{tank} refer to the reactant concentration in the cell and the tank, respectively.

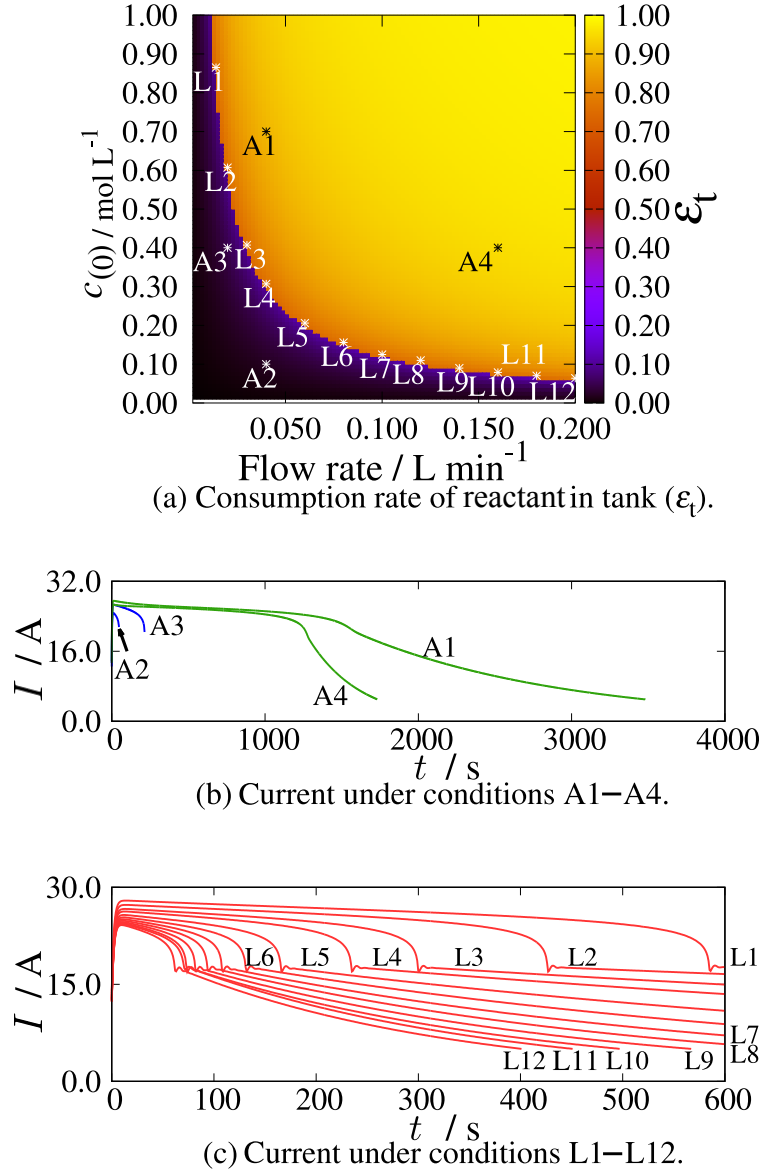


Figure 3.3: Discharging behavior classified into three cases. (a) Consumption rate of reactant in tank for each condition. The yellow area represents the conditions for which the reactant in the tank is consumed. (b) Current under conditions A1–A4. The discharging for the conditions A1 and A4 are classified into Case2. The conditions A2 and A3 give the discharging behavior classified into Case1. (c) Current under conditions L1–L12. The discharging behavior is classified into Case3.

as well as the simulation result for $W = 0.050 \text{ Lmin}^{-1}$, $c(0) = 0.125 \text{ molL}^{-1}$ in Figure 3.2. The current and the voltage drop quickly, and a lot of reactant remain in the tank until the finish of discharging. The short discharging without consuming the reactant in the tank is classified into Case 1. The discharging behavior under the conditions A1 and A4 is similar to the simulation result for $W = 0.200 \text{ Lmin}^{-1}$, $c(0) = 0.125 \text{ molL}^{-1}$ in Figure 3.2. The discharging continues for a long duration, and the reactant in the tank is consumed. The oscillation does not appear in the current and the voltage. The long discharge without the oscillation is classified into Case 2. As Figure 3.3(c) shows, the oscillation appears when the conditions are set at L1–L12. L1–L12 are located upon the boundary. The long discharging behavior with oscillation is classified into Case 3.

3.2 Dynamical mechanism of discharging

There seems to exist a mechanism governing the three types of discharging behaviors. The understanding of the mechanism contributes to verifying the simulation results. This section is going to clarify the dynamics governing the discharging behaviors in the simulation.

3.2.1 Dimensionless state equation for analysis

Subsection 3.2.1 introduces a dimensionless state equation. The discharging behaviors are governed by the time evolution of three state variables: the reactant concentration in the cell, the change rate of reactant concentration, and the current. The time evolution of the state variables is given by ODEs (3.2) and (3.3). The state variables have different scales. These state variables are normalized for analyzing the dynamics, and the dimensionless state equation is introduced from ODEs (3.2) and (3.3).

The state variables and the time are normalized as equation (3.7)

$$x_1 = \frac{c(t)}{\hat{c}}, \quad x_2 = \frac{dc(t)}{dt} \frac{\hat{t}}{\hat{c}}, \quad x_3 = \frac{I(t)}{\hat{I}}, \quad \tau = \frac{t}{\hat{t}} \quad (3.7)$$

Where x_1 , x_2 , and x_3 are the dimensionless variables corresponding to c , dc/dt , and I . τ is the normalized time. The constants for the normalization are given by

following equation (3.8).

$$\hat{c} = c_{\max}, \hat{t} = \sqrt{\frac{\alpha_c F L c_{\max}}{E_{\text{eh}}^0}}, \hat{I} = \frac{E_{\text{eh}}^0}{r + r_{\text{rfb}}} \quad (3.8)$$

The dimensionless state equation is introduced from ODEs (3.2) and (3.3) as follows.

$$\begin{cases} \frac{dx_1}{d\tau} &= x_2 \\ \frac{dx_2}{d\tau} &= -\beta x_2 + (1 - \gamma)x_3 - \left(1 + \delta \ln \frac{x_1}{1 - x_1}\right) \\ \varepsilon \frac{dx_3}{d\tau} &= -x_3 + 1 + \delta \ln \frac{x_1}{1 - x_1} \end{cases} \quad (3.9)$$

This state equation includes the nonlinear terms, and they are derived from Nernst equation (2.7). The parameters β , γ , δ , and ε are given by equation (3.10).

$$\beta = W \left(\frac{1}{\alpha_c} + \frac{1}{\alpha_t} \right) \hat{t}, \quad \gamma = \frac{WL}{\alpha_t(r + r_{\text{rfb}})}, \quad \delta = \frac{2RT}{FE_{\text{eh}}^0}, \quad \hat{t}' = \frac{L}{(r + r_{\text{rfb}})}, \quad \varepsilon = \frac{\hat{t}'}{\hat{t}} \quad (3.10)$$

The more detailed process for introducing dimensionless state equation (3.9) is explained in Appendix A.

3.2.2 Analysis in neighborhood of the fixed point

Subsection 3.2.2 studies the dynamics of the system governed by the dimensionless state equation (3.9) in the neighborhood of the fixed point. State equation (3.9) includes the nonlinear terms. The dynamics of nonlinear systems are often analyzed in the neighborhood of the fixed point [68]. The system is linearized around the fixed point, and the local stability of the fixed point is investigated from the eigenvalues of the linearized system.

The fixed point of the system is given by $d\mathbf{x}/d\tau = \mathbf{0}$ ($\mathbf{x} = [x_1 \ x_2 \ x_3]^T$). The system has only one fixed point $\mathbf{x}^* = [3.51 \times 10^{-12} \ 0 \ 0]^T$. The fixed point corresponds to the state at which the EMF, the change rate of reactant concentration, and the current are 0.

Table 3.2: Eigenvalues of Jacobian matrix A . The negative real parts imply that the fixed point $\mathbf{x}^*$ is locally stable.

$W(\text{Lmin}^{-1})$	Eigenvalues of Jacobian matrix A
0.050	$-8.70 + 1.49 \times 10^5 j$ $-8.70 - 1.49 \times 10^5 j$ -3.17×10^{-2}
0.100	$-8.84 + 1.49 \times 10^5 j$ $-8.84 - 1.49 \times 10^5 j$ -6.34×10^{-2}
0.200	$-9.13 + 1.49 \times 10^5 j$ $-9.13 - 1.49 \times 10^5 j$ -12.7×10^{-2}

Dimensionless state equation (3.9) is linearized around the fixed point as follows.

$$\Delta \mathbf{x} = A \Delta \mathbf{x}, \quad (3.11)$$

$$A = \begin{bmatrix} 0 & 1 & 0 \\ -f(x_1^*) & -\beta & 1 - \gamma \\ f(x_1^*)/\varepsilon & 0 & -1/\varepsilon \end{bmatrix}, \quad f(x_1) = \frac{\delta}{x_1(1 - x_1)}$$

Here, $\Delta \mathbf{x} = \mathbf{x} - \mathbf{x}^*$. $f(x_1)$ is the linearized form of the normalized Nernst equation.

Table 3.2 shows the eigenvalues of A for $W = 0.050 \text{ Lmin}^{-1}$, 0.100 Lmin^{-1} , and 0.200 Lmin^{-1} . For these three parameters, the real parts of eigenvalues are negative, and the fixed point $\mathbf{x}^*$ is locally stable. The states in the neighborhood of the fixed point converge to the fixed point. Moreover, the states oscillate around the fixed point in approaching the fixed point.

Figure 3.4 illustrates the state trajectories in the phase space. The trajectory corresponding to Case 1 is described with the blue hashed line and does not converge to the fixed point. The trajectory corresponding to Case 3 is described with the red

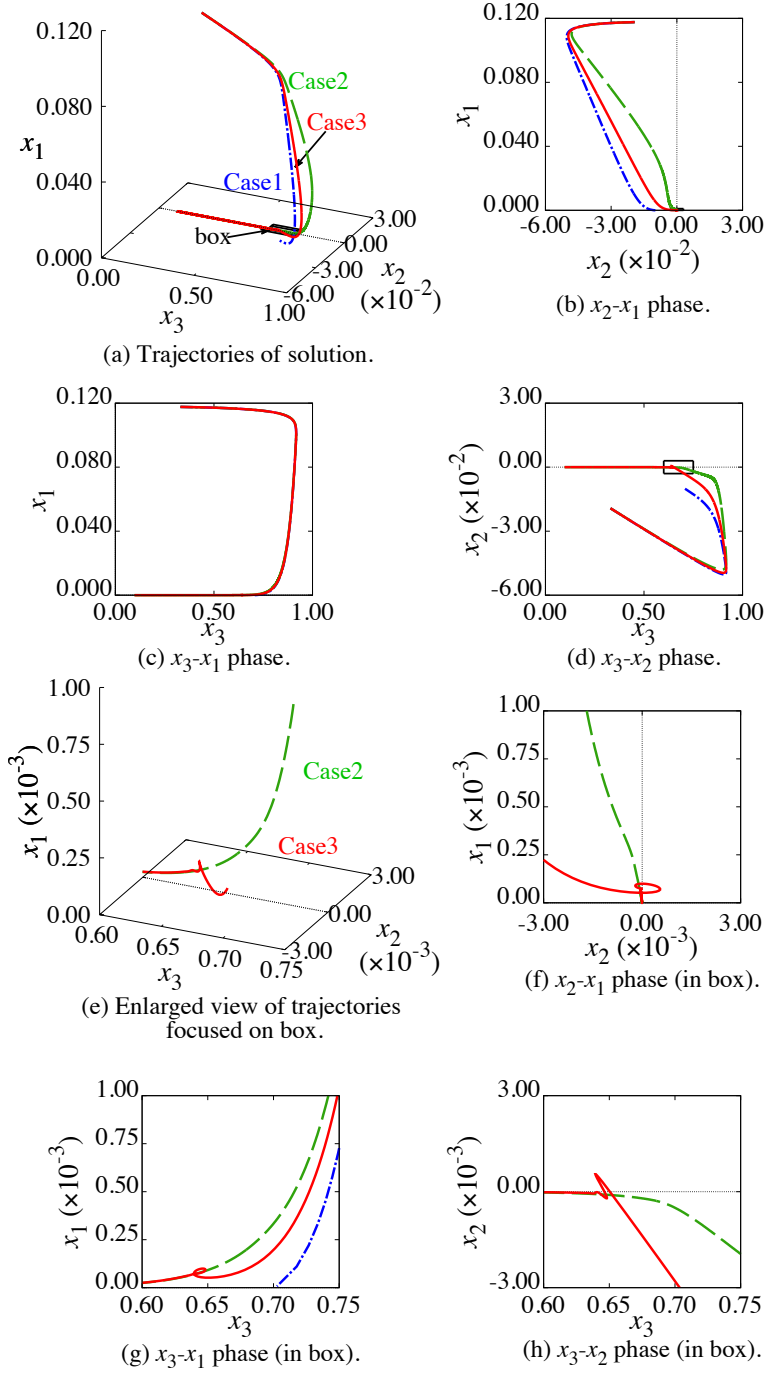


Figure 3.4: State trajectories in phase space. Each trajectory refers to the different discharging behavior. x_1 is the normalized reactant concentration. x_2 is the normalized change rate of reactant concentration. x_3 is the normalized current. (e)–(h) Enlarged view of the trajectories.

line and does not oscillate around the fixed point. These trajectories suggest that the difference in the discharging behaviors is not derived from the dynamics in the neighborhood of the fixed point.

3.2.3 Global phase structure

This subsection discusses a part of the global phase structure of the solutions for analyzing the dynamics apart from the fixed point. The global phase structure is magnified at a small scale for visualizing the vector field.

Figure 3.5(a) shows a part of the trajectories in the phase space. The flow rate is fixed at $W = 0.100 \text{ Lmin}^{-1}$, and the trajectories are given by shifting the initial value of the reactant concentration in the cell. In this figure, the oscillations are found in $x_1 \sim 10^{-4}$. The scale of changes in x_3 is much bigger than both x_1 and x_2 . This implies the x_3 is sensitive to the variation in x_1 and x_2 for $x_1 \sim 10^{-4}$.

The trajectories are projected on the planes in Figures 3.5(b)–(j), and the manifolds referring to $dx_i/d\tau = 0$ ($i = 1, 2, 3$) are illustrated on each plane. The trajectories converge to $dx_1/d\tau=0$, $dx_2/d\tau=0$, and $dx_3/d\tau=0$. The oscillations appear in approaching these manifolds.

The vector field shows the dynamics around the manifolds in the phase space. As Figure 3.5(b) shows, the vector field accelerates the decrease of x_1 on the plane $x_2 = -2.0 \times 10^{-3}$. As a result, some trajectories go out of the domain $x_1 > 0$ before they reach the manifolds. These trajectories correspond to the discharging behavior classified into Case 1. On the other hand, Figure 3.5(c) shows the trajectories corresponding to Case 2 and Case 3 are driven by the vector field and converge to $dx_3/d\tau=0$ on the plane $x_2 = 0$.

The fast flow along x_3 in Figure 3.5(c) also indicates that this system is similar to the slow-fast system [69, 70], and $dx_3/d\tau=0$ is the fast manifold. $\varepsilon \ll 1$ in equation (3.9), and $|dx_1/d\tau|, |dx_2/d\tau| \ll |dx_3/d\tau|$. x_1 and x_2 can be seen as the slow variables.

Figures 3.5(e)–(j) shows that the trajectories also approach $x_2(= dx_1/d\tau)=0$ in addition to $dx_3/d\tau = 0$. The vector field on Figures 3.5(e)–(g) shows that the flow along with x_1 is slow with comparison to x_2 . It is indicated that x_1 is the slowest state variable.

The mechanism of the oscillations can be discussed by fixing the flow along with x_1 . Dimensionless state equation (3.9) is linearized around the fixed x_1 as well as

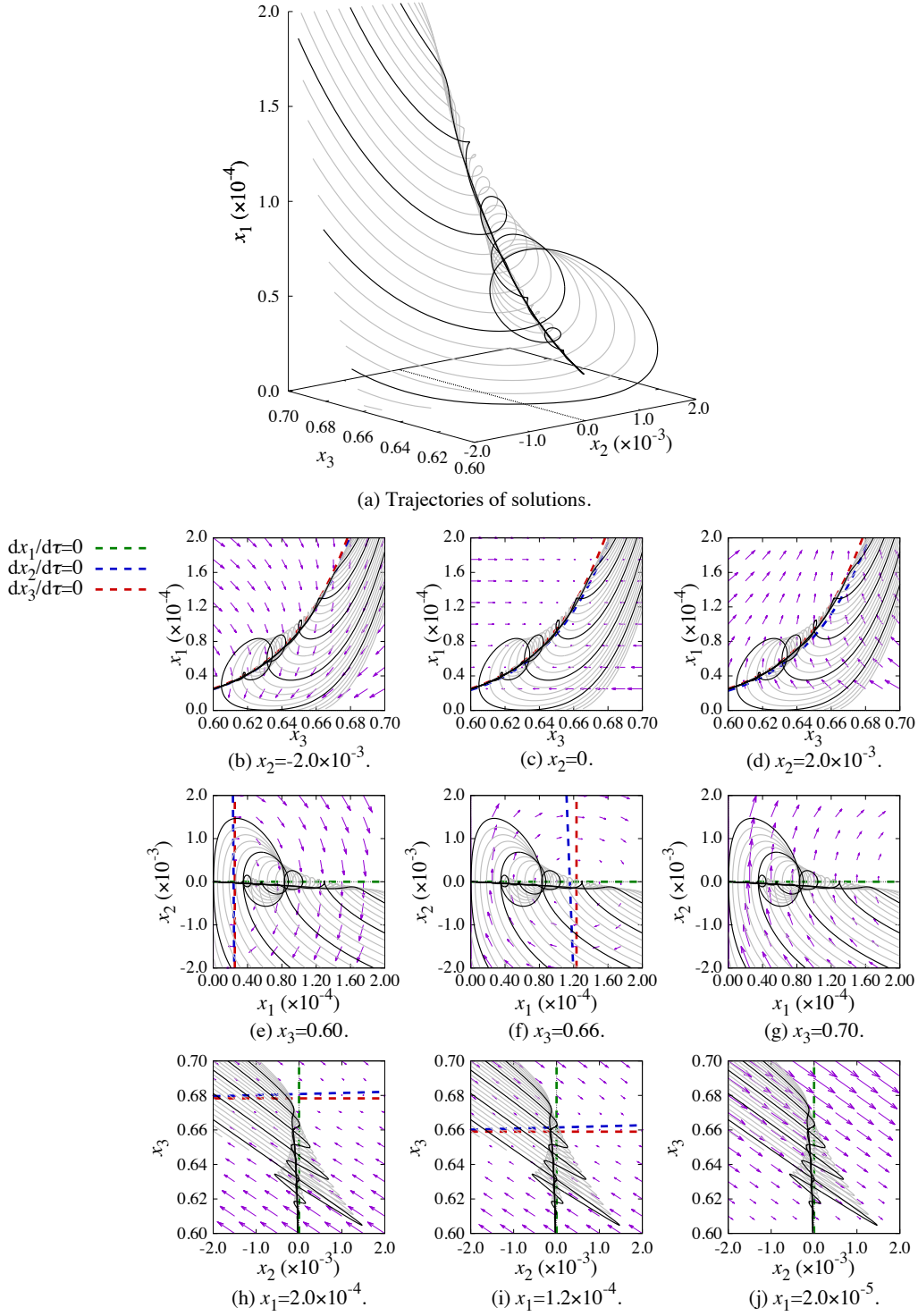


Figure 3.5: Global phase structure of solutions and vector field at $W = 0.100 \text{ Lmin}^{-1}$. The area where the oscillation occurs is focused on. The trajectories are given by shifting the initial value of the reactant concentration in the cell. (b)–(j) Vector field and projected trajectories.

the analysis in Subsection 3.2.2, x_1 is swapped in $f(x_1)$ from $x_1=0.01 \times 10^{-4}$ to $x_1=50.00 \times 10^{-4}$, and Jacobian matrix A' is given.

The eigenvalues of A' are shown in Figures 3.7(a) and (b). The eigenvalues are located on the complex plane with $\text{Re}[\lambda_i] < 0$ ($i = 1, 2, 3$). Then, a bifurcation appears at $x_1=5.72 \times 10^{-4}$. The eigenvalues become real in $x_1 > 5.72 \times 10^{-4}$, and there does not appear any oscillatory discharging behaviors. λ_1 and λ_2 come close to each other as x_1 decreases, and λ_1 and λ_2 conjoint at $x_1 = 5.72 \times 10^{-4}$. After the conjoint, λ_1 and λ_2 apart with the imaginary parts. The oscillation can appear in $x_1 < 5.72 \times 10^{-4}$. Almost all λ_1 and λ_2 distribute in $|\text{Im}[\lambda_i]| < 50$ ($i = 1, 2$). The period of the oscillation in the original scale is estimated as $T_p > 2\pi/50 \times \hat{t} = 4\text{ s}$.

Figure 3.6(c) shows the phase lags of λ_i ($i = 1, 2, 3$). The lags converge to 90 deg, 90 deg, and 180 deg with $x_1 \rightarrow 0$. Then, the phase lags of the oscillations are also expected to converge 90 deg, 90 deg, and 180 deg. Actually, in Figures 3.4(b)–(j), the oscillation in x_1 has about 90 deg phase lag to x_2 and x_3 , and the oscillation in x_2 has about 180 deg phase lag to x_3 . The phase lag appears in Figure 3.6(c) indicates that the eigenvalues in Figure 3.6 certainly shows the mechanism of the oscillation.

3.2.4 Behavior in the original scale

Subsection 3.2.4 discusses the validity of the analysis in Subsections 3.2.2 and 3.2.3 with the time evolution of the variables on the original scale. Figures 3.7(a)–(c) show $c(t)$, $dc(t)/dt$, and $I(t)$ in the original scale.

The analysis in Subsection 3.2.2 denies the effect of the dynamics around the fixed point on the discharging behaviors. Figure 3.4 also proves that the three types of discharging behaviors are not governed by the dynamics in the neighborhood of the fixed point. The fixed point corresponds to the state at which $c = 5.97 \times 10^{-12} \text{ molL}^{-1}$, $dc/dt = 0$, and $I = 0$. Some solutions do not reach the fixed point, as well as Figures 3.4(a)–(d). Moreover, the solutions do not oscillate around the values corresponding to the fixed point. The oscillation occurs for $c \sim 10^{-5} - 10^{-4} \text{ molL}^{-1}$ and $I \sim 10\text{ A}$.

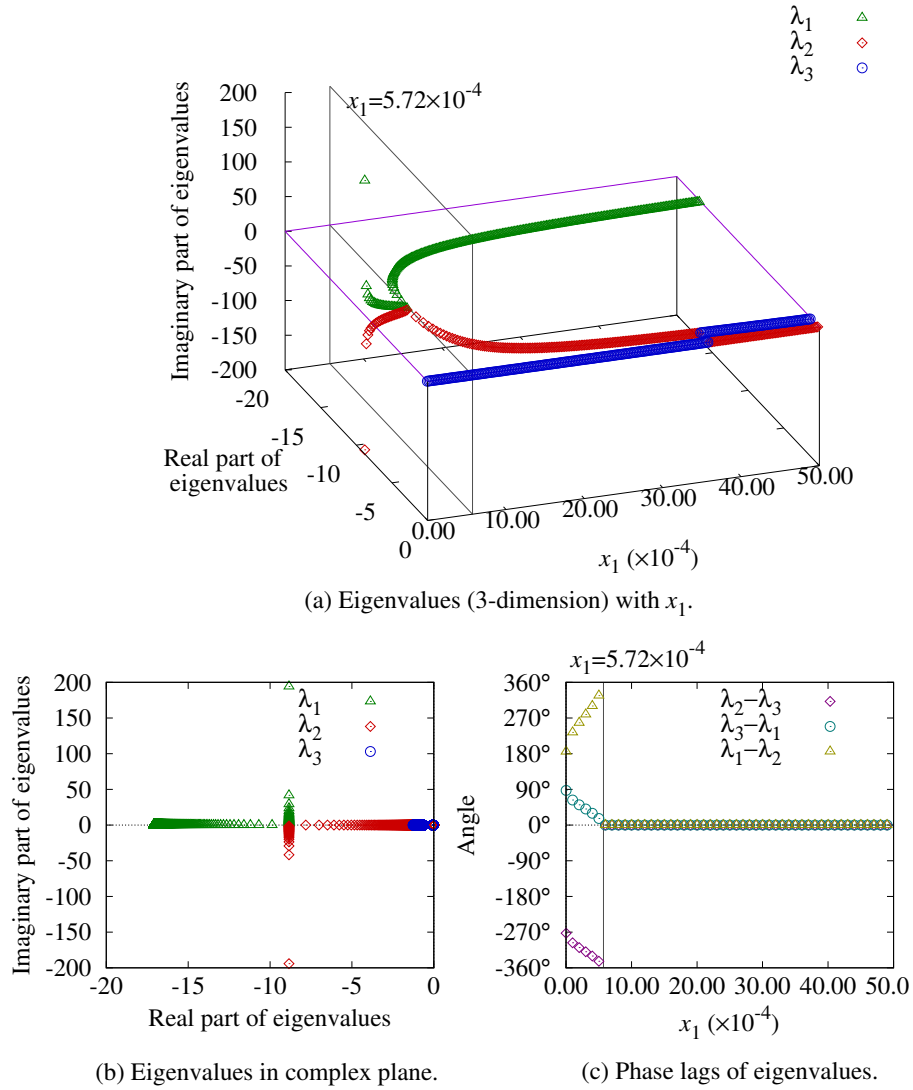


Figure 3.6: Eigenvalues of Jacobian matrix A' . (a) Eigenvalues with fixed x_1 . A bifurcation appears at $x_1 = 5.72 \times 10^{-4}$. In $x_1 < 5.72 \times 10^{-4}$, imaginary part appears. (b) Eigenvalues in complex plane. (c) Phase lags of eigenvalues λ_i ($i = 1, 2, 3$).

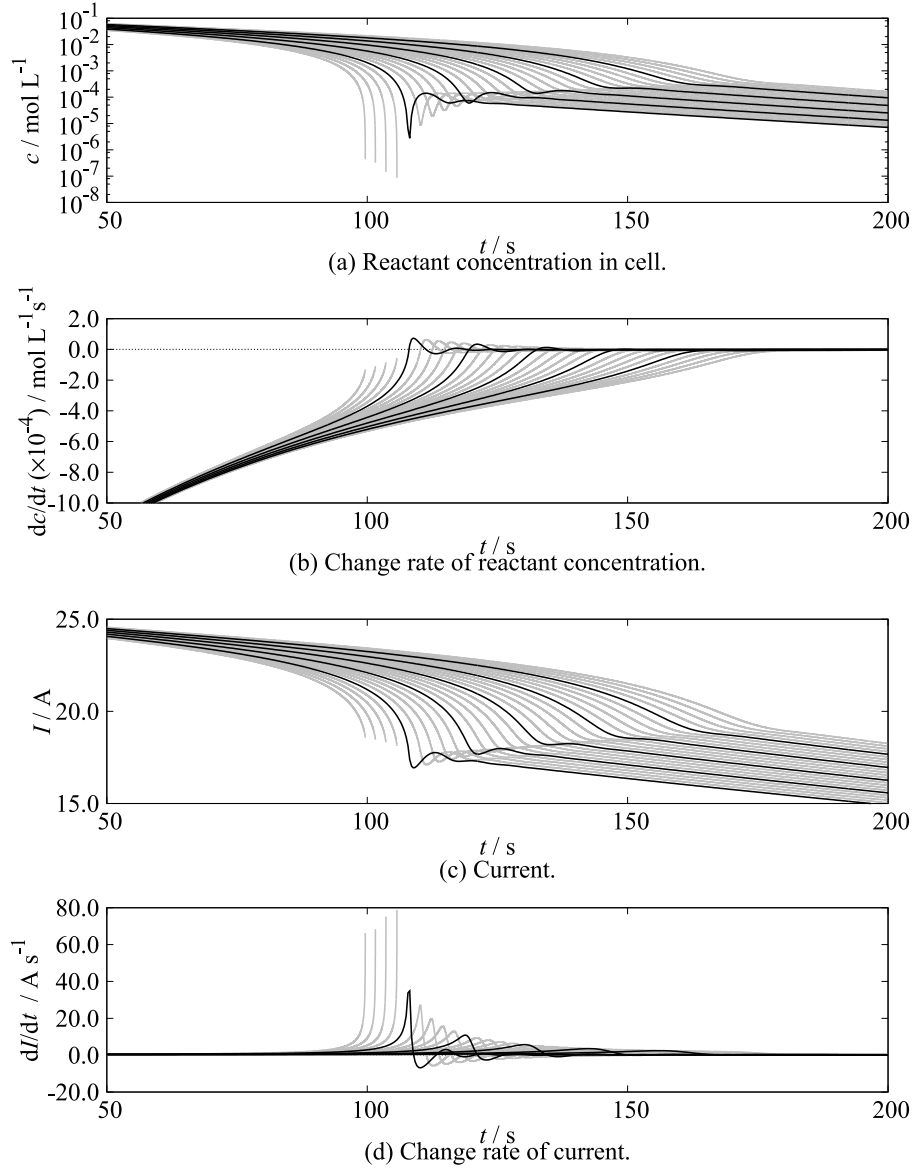


Figure 3.7: Time evolution of state variables in original scale. The flow rate of the electrolyte is fixed for $W = 0.100 \text{ Lmin}^{-1}$ and the initial value of c is shifted.

$dc(t)/dt$ oscillates around $dc/dt = 0$. The trajectories in Figure 3.4 also oscillate while approaching $dx_2/d\tau = 0$. The difference in the discharging behaviors appears in approaching $dc/dt = 0$. Considering the mass balance of the reactant in the cell, the restriction to $dc/dt = 0$ indicates that the current is restricted by the mass transport from the tank to the cell.

Figure 3.7(d) shows $dI(t)/dt$. The cell discharges while being restricted to $dI/dt = 0$ in all three cases. $dI/dt = 0$ is corresponding to $dx_3/d\tau = 0$ in Figure 3.4 and represents the steady-state of the current in the electrical circuit. The restriction is derived from the feature of the system as a slow-fast system, and the electrical circuit is regarded as the fast-subsystem.

The period of the oscillation is estimated as $T_p > 4$ s from the imaginary part of the eigenvalues in Figure 3.6(b). The period of the oscillation in the original scales is about 10 s, and the order is not so different from the value estimated from the eigenvalues.

3.3 Summary

This chapter studies the discharging behavior due to the dynamic change of current, and the dynamical mechanism is analyzed. Different discharging behaviors appear depending on the flow rate of the electrolyte and the initial condition. The difference appears for the low concentration of the reactant in the cell.

The analysis shows that the global phase structure governs the discharging behavior. The feature of the slow-fast system is found in the analysis. The target system can be linearized by taking the perpendicular plane to the slow variable, and the Jacobian matrix shows the necessary condition for the occurrence of the oscillations.

The discharging behavior in the simulation gives a critical direction in the operation of the RFB. As the worst case, the slow rate of mass transport leads to the depletion of the reactant in the cell. The discharging and the power supply stop without consuming the reactant in the tank. The simulation also indicates that the current is restricted by mass transport for the higher rate of mass transport. Moreover, there are conditions that arise oscillations. It may cause resonances with external systems. To avoid these anomalous phenomena, a control method of multiple layers must be developed with considering chemical, fluid dynamics, and electrical circuit restriction.

The difference in the discharging behaviors appears in approaching the state, at which the current is restricted by the mass transport. Chapter 5 introduces the indicator for extracting this state and proposes the method for predicting the occurrence of the current-restriction by the mass transport.

Chapter 4

Model with transport delay for large RFB system

Chapter 4 introduces the model with transport delay. The transport time is known to appear as a delay in the dynamics of fluid systems, including the district heating system [71] and the exhaust gas recirculation engine [72]. The effect of the delay has been analyzed for controlling the fluid systems [71–73]. The transport delay is also expected to appear in the charging/discharging dynamics of the cells in the RFBs. The RFBs also require the model considering the transport delay for analyzing its effect. Section 4.1 shows the charging/discharging behavior of a proto-type RFB in an experiment. The voltage of the proto-type RFB is affected by the delay derived from the circulation system of the electrolytes. Section 4.2 develops the model from the mass balance equations in Chapter 2. The model is verified by comparing the simulation results with the experimental results.

4.1 Detection of delay derived from circulation system

4.1.1 Monitor cell for detecting delay

Subsection 4.1.1 explains the method for detecting the delay derived from the circulation system in the experiment. This experiment employs the proto-type RFB equipped with a monitor cell. Conventionally, the monitor cell has been integrated to RFBs for estimating the SOC of the other cells [38, 74]. But, this chapter uses

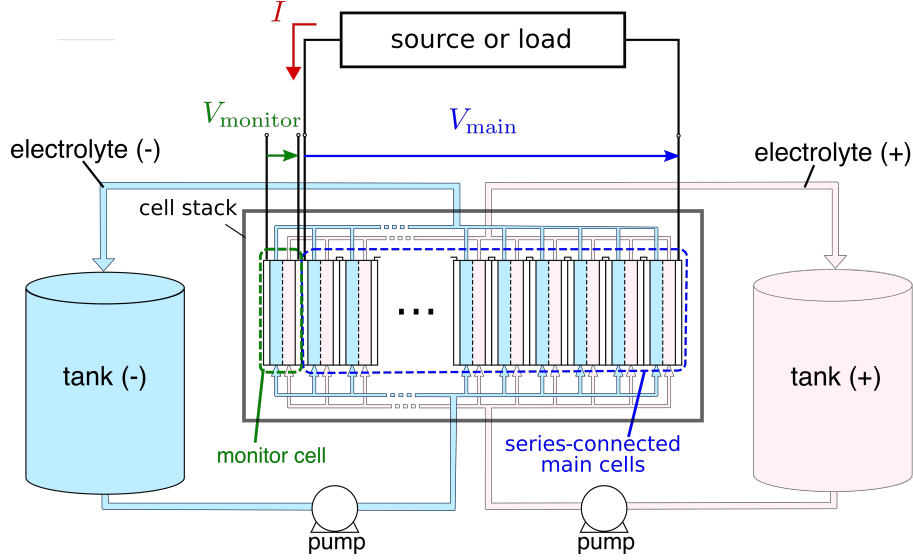


Figure 4.1: RFB system equipped with monitor cell. The main cells are connected in series. The port of the monitor cell is opened. The electrolytes flow through all of the cells in parallel. V_{main} is the total voltage of the main cells. V_{monitor} is the voltage of the monitor cell, which shows the EMF. I is the current.

the monitor cell for detecting the delay derived from the circulation system of the electrolytes.

Figure 4.1 shows an RFB system equipped with the monitor cell. The cell stack consists of the series-connected main cells and the monitor cell. The electrolytes flow through these cells in parallel. The main cells are connected to a source or a load, and the current flows into the main cells. The port of the monitor cell is opened, the redox reaction does not occur in the monitor cell. The EMF is measured from the open port of the monitor cell.

Figure 4.2 explains the delay derived from the circulation system. If the disturbance occurs in the current at $t = t_0$, the effect of the disturbance appears in the charging/discharging dynamics of the cells with a delay t_d . The delay t_d is derived from the mass transport via the pipes and the stay in the tank. The significant delay appears in the monitor cell because the dynamics of the monitor cell are only governed by the mass transport.

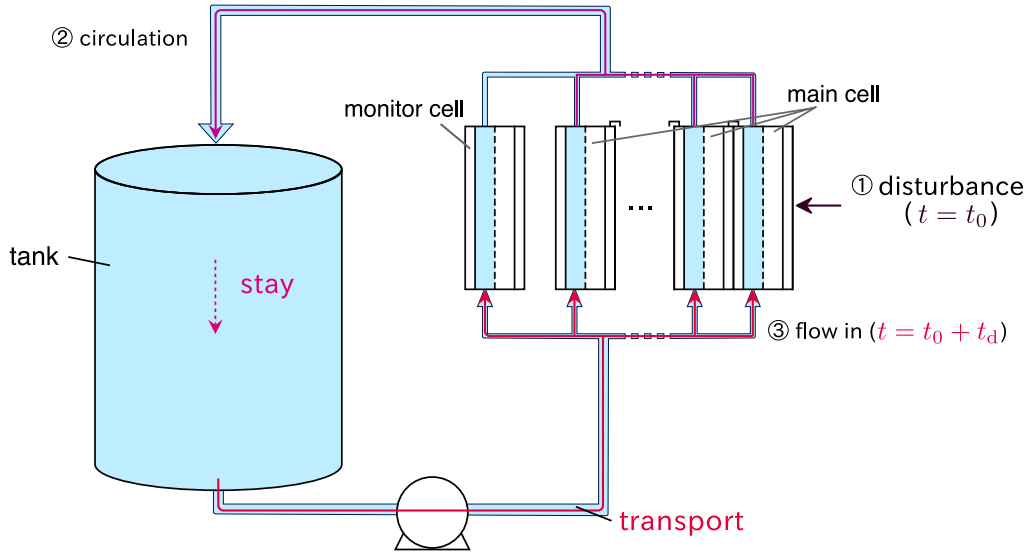


Figure 4.2: Delay derived from circulation system of electrolyte. ① The disturbance occurs in the current at $t = t_0$. ② The electrolyte circulates. ③ The effect of the disturbance appears at $t = t_0 + t_d$. The charging/discharging of the monitor cell is only governed by mass transport and clearly reflects the delay.

4.1.2 Experimental setup

Figure 4.3 shows the experimental setup. The cell stack in the proto-type RFB is connected to the external circuit in the experimental setup. The parameters for the proto-type RFB are listed in Table 4.1.

The proto-type RFB consists of the cell stack and one couple of the tanks. As Figure 4.3(b) shows, ten main cells and one monitor cell are stacked. The flow rate of the electrolytes at the inlet of the cell stack is written in Table 4.1.

Figure 4.3(c) shows the configuration of the external circuit. This circuit includes a charging/discharging controller, a DC supply (MATSUSADA PQ-20-60), a switcher, and a load. The DC supply is set at the constant current mode. The controller switches the direction of the current flowing into the main cells.

The proto-type RFB charged and discharged at the fixed current. For $t < 0$, there was no current, and the reactant was distributed in the proto-type RFB uniformly. The main cells were connected to the DC supply for $t \geq 0$, and they began to charge at $t = 0$. The direction of the current was switched instantly when the total voltage of the main cells reached the threshold. The main cells began to

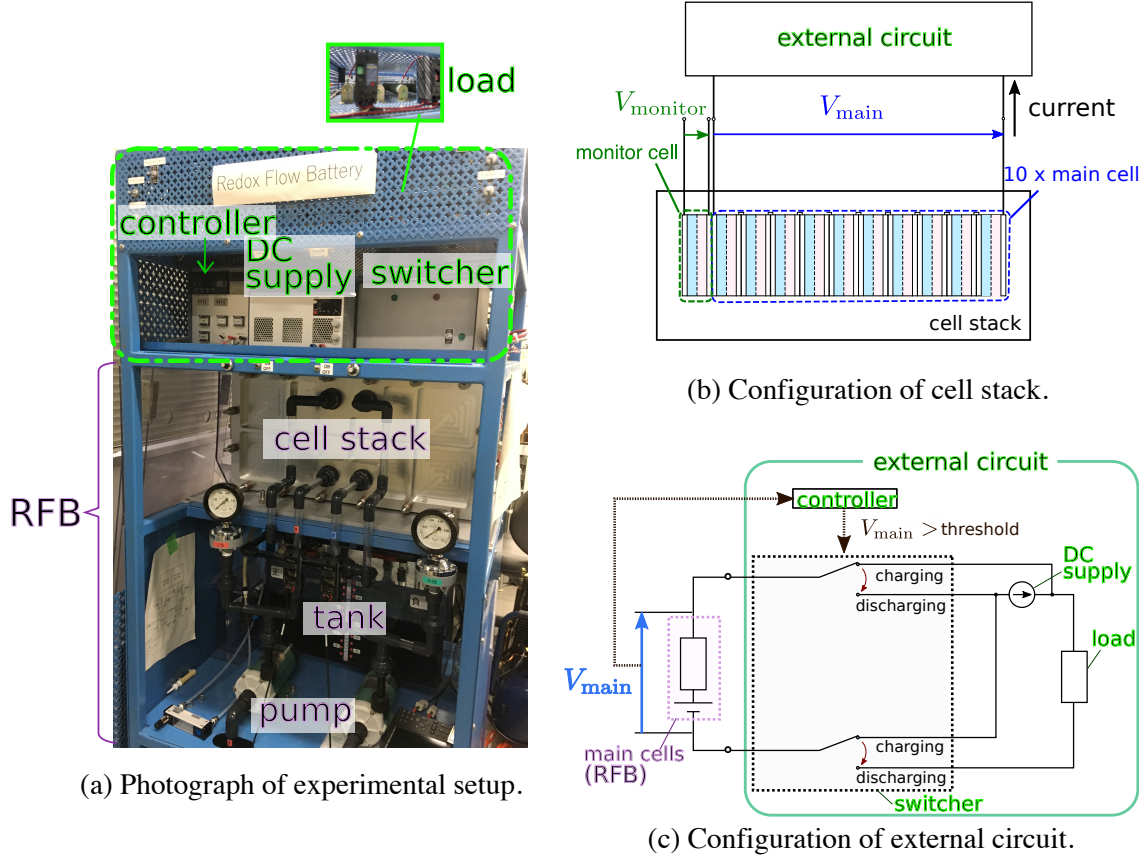


Figure 4.3: Experimental setup. (a) Photograph of experimental setup. (b) Configuration of cell stack in proto-type RFB. The cell stack consists of ten main cells and one monitor cell. The series-connected main cells are loaded. The monitor cell has no load. (c) Configuration of external circuit with proto-type RFB. The DC supply (MATSUSADA PQ-20-60) and the load enable the proto-type RFB to charge/discharge for fixed current. First, the proto-type RFB was charged by the DC supply. When the voltage of the main cells reached the threshold, the circuit was switched by the controller. The proto-type RFB began to discharge.

Table 4.1: Parameters for experiment.

Current (I)	-50 A or 50 A
Threshold of V_{main}	14.50 V
Number of main cells (m)	10
Flow rate of electrolytes at inlet of cell stack	$3.3 \text{ Lmin}^{-1}/5.5 \text{ Lmin}^{-1}$
Volume of each cell	125 mL
Volume of each tank	10 L

discharge after the switching.

4.1.3 Voltage of main cells and monitor cell in experiment

Figures 4.4(a) and (b) show the voltage of the main cells and the monitor cell. Both the main cells and the monitor cell switch their mode from charging to discharging, and there appears a delay. The length of the delay varies depending on the flow rate of the electrolytes, and the delay is derived from the circulation system.

The experimental result also denies the condition for estimating the SOC with the monitor cell. The SOC of the monitor cell can be estimated from the voltage of the monitor cell under the following condition (ref. Appendix B).¹

$$\begin{aligned}
 c_{\text{main}} &\in \mathbb{A}, \\
 \mathbb{A} &= \{c_{\text{main}} \in (0, c_{\text{max}}) \mid |g(c_{\text{main}}) - g(c_{\text{monitor}})| < \varepsilon_e\}
 \end{aligned} \tag{4.1}$$

$g(c_i)$ ($i = \text{main}, \text{monitor}$) gives the EMF of each cell. Condition (4.1) assures that the difference of the reactant concentration between the main cells and the monitor cell is small enough not to affect the estimation. The following relationship is also satisfied under condition (4.1).

$$\begin{aligned}
 \Delta V(t) &= V_{\text{main}}(t)/m - V_{\text{monitor}}(t) \\
 &= \{g(c_{\text{main}}(t)) - r_{\text{rfb}}I\} - g(c_{\text{monitor}}(t)) \\
 &\approx -r_{\text{rfb}}I
 \end{aligned} \tag{4.2}$$

¹The order of ε_e is about 0.01 V in the experiment.

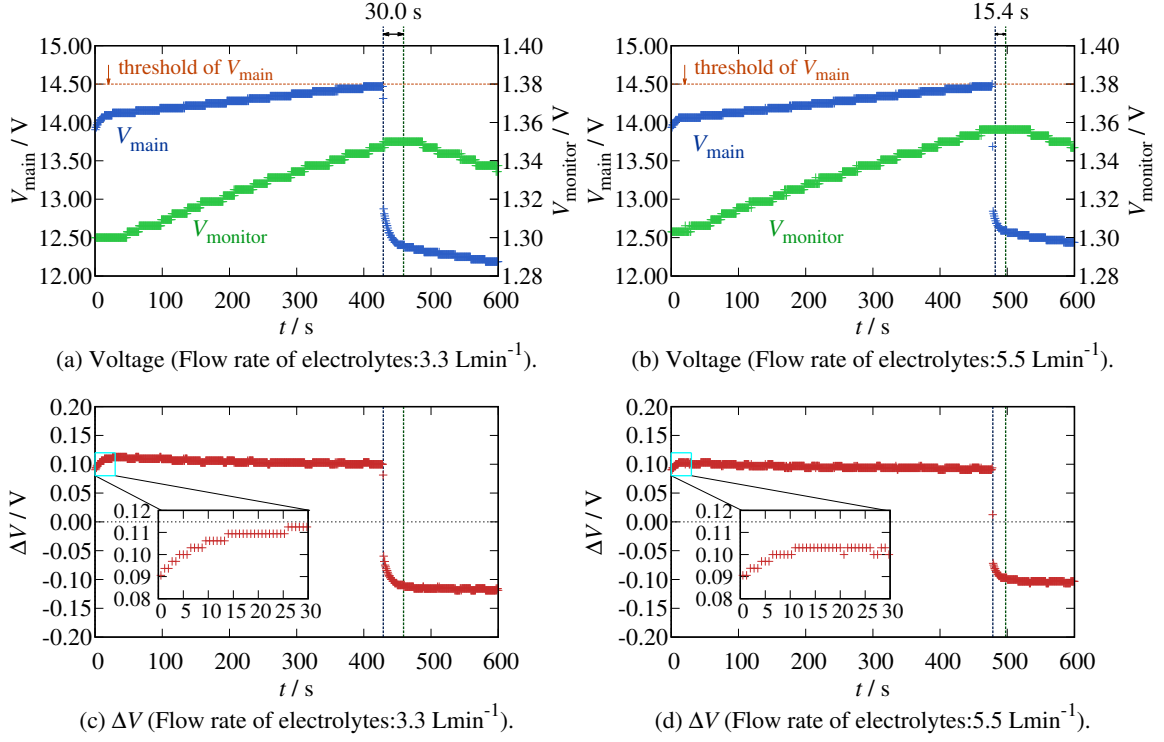


Figure 4.4: Voltage of cells affected by delay derived from circulation system in experiment. 3.3 Lmin⁻¹ and 5.5 Lmin⁻¹ are the flow rate of the electrolytes at the inlet of the cell stack. (a), (b) Total voltage of main cells and voltage of monitor cell. The monitor cell switches its operational mode with a delay of 30.0 s or 15.4 s to main the cells. (c), (d) Difference between the averaged voltage of the main cells and the voltage of the monitor cell ($\Delta V(t) = V_{\text{main}}(t)/m - V_{\text{monitor}}(t)$). m is the number of the main cells.

Here, ΔV refers to the difference between the averaged voltage of the main cells and the voltage of the monitor cell. m is the number of the main cells, and r_{rfb} is the internal resistance. The current is fixed in this experiment, and a stepping change is expected to appear in $\Delta V(t)$. However, $\Delta V(t)$ seems to behave according to a first-order lag system in Figures 4.4(c) and (d). The curve in $\Delta V(t)$ denies condition (4.1).

4.2 Description of charging/discharging with DDE

4.2.1 Introduction of model

Subsection 4.2.1 introduces the model for simulating the charging/discharging behavior of the proto-type RFB, which is affected by the delay derived from the circulation system. The differential equation of the reactant concentration in each cell is developed from mass balance equations (2.14)–(2.16) in Chapter 2. The voltage is given by fundamental equations (2.7) and (2.12).

Considering the structure of the proto-type RFB in Figure 4.3(b), the mass balance equations in each main cell, the monitor cell, and the RFB are rewritten as equations (4.3)–(4.5).

$$\frac{dc_{\text{main}}(t)}{dt} = -\frac{I(t)}{\alpha_c F} + \frac{W}{\alpha_c} \{c_{\text{tank}}(t - \tau_d) - c_{\text{main}}(t)\} \quad (4.3)$$

$$\frac{dc_{\text{monitor}}(t)}{dt} = \frac{W}{\alpha_c} \{c_{\text{tank}}(t - \tau_d) - c_{\text{monitor}}(t)\} \quad (4.4)$$

$$\frac{dN(t)}{dt} = -\frac{mI(t)}{F} \quad (4.5)$$

The first terms in mass balance equations (4.3) and (4.5) correspond to the rate of the redox reaction. The other term represents the reactant flow. W is the flow rate of the electrolyte in each cell.

α_c is the volume of the electrolyte in each half cell. τ_d is the transport time from the tank to the cells. $N(t)$ is the molar amount of reactants in the RFB, which is given by equation (4.6).

$$N(t) = m\alpha_c c_{\text{main}}(t) + \alpha_c c_{\text{monitor}}(t) + \alpha_t c_{\text{tank}}(t) \quad (4.6)$$

α_t is the volume of the electrolyte in each tank.

Suppose that mass balance equations (4.3) and (4.4) are differentiable as follows.

$$\frac{d^2 c_{\text{main}}(t)}{dt^2} = -\frac{1}{\alpha_c F} \frac{dI(t)}{dt} + \frac{W}{\alpha_c} \left\{ \frac{d}{dt} c_{\text{tank}}(t - \tau_d) - \frac{d}{dt} c_{\text{main}}(t) \right\} \quad (4.7)$$

$$\frac{d^2 c_{\text{monitor}}(t)}{dt^2} = \frac{W}{\alpha_c} \left\{ \frac{d}{dt} c_{\text{tank}}(t - \tau_d) - \frac{d}{dt} c_{\text{monitor}}(t) \right\} \quad (4.8)$$

$dc_{\text{tank}}(t)/dt$ is given by differentiating equation (4.6).

$$\begin{aligned} \frac{dN(t)}{dt} &= m\alpha_c \frac{dc_{\text{main}}(t)}{dt} + \alpha_c \frac{dc_{\text{monitor}}(t)}{dt} + \alpha_t \frac{dc_{\text{tank}}(t)}{dt} \\ \frac{dc_{\text{tank}}(t)}{dt} &= \frac{1}{\alpha_t} \frac{dN(t)}{dt} - \frac{m\alpha_c}{\alpha_t} \frac{dc_{\text{main}}(t)}{dt} - \frac{\alpha_c}{\alpha_t} \frac{dc_{\text{monitor}}(t)}{dt} \\ &= -\frac{mI(t)}{\alpha_t F} - \frac{m\alpha_c}{\alpha_t} \frac{dc_{\text{main}}(t)}{dt} - \frac{\alpha_c}{\alpha_t} \frac{dc_{\text{monitor}}(t)}{dt} \end{aligned} \quad (4.9)$$

The DDEs as the model equations are introduced as following equations (4.10) and (4.11) by substituting equation (4.9) to equations (4.7) and (4.8).

$$\begin{aligned} \frac{d^2 c_{\text{main}}(t)}{dt^2} &= -\frac{W}{\alpha_c} \frac{dc_{\text{main}}(t)}{dt} - \frac{mW}{\alpha_t} \frac{dc_{\text{main}}(t - \tau_d)}{dt} \\ &\quad - \frac{W}{\alpha_t} \frac{dc_{\text{monitor}}(t - \tau_d)}{dt} - \frac{mWI(t - \tau_d)}{\alpha_c \alpha_t F} - \frac{1}{\alpha_c F} \frac{dI(t)}{dt} \end{aligned} \quad (4.10)$$

$$\begin{aligned} \frac{d^2 c_{\text{monitor}}(t)}{dt^2} &= -\frac{W}{\alpha_c} \frac{dc_{\text{monitor}}(t)}{dt} - \frac{mW}{\alpha_t} \frac{dc_{\text{main}}(t - \tau_d)}{dt} \\ &\quad - \frac{W}{\alpha_t} \frac{dc_{\text{monitor}}(t - \tau_d)}{dt} - \frac{mWI(t - \tau_d)}{\alpha_c \alpha_t F} \end{aligned} \quad (4.11)$$

DDEs (4.10) and (4.11) include τ_d as the delay.

The voltage of the cells can be obtained by substituting the solution of DDEs (4.10) and (4.11) into the following equations.

$$V_{\text{main}}(t) = m\{g(c_{\text{main}}(t)) - r_{\text{rfb}}I(t)\}, \quad V_{\text{monitor}}(t) = g(c_{\text{monitor}}(t)) \quad (4.12)$$

4.2.2 Comparison of simulation and experiment

Subsection 4.2.2 verifies that the DDEs can reproduce the charging/discharging behavior of the proto-type RFB. The simulation results are compared to the experimental data.

Table 4.2: Parameters for simulations.

W	Flow rate of electrolyte in each cell	0.3 Lmin^{-1}	0.5 Lmin^{-1}
α_t	Volume of electrolyte in each tank	8.74 L	8.44 L
α_c	Volume of electrolyte in each half cell	0.045 L	0.045 L
τ_d	Transport delay (transport time)	19.0 s	15.0 s
r_{fb}	Internal resistance (charging)	$1.8 \text{ m}\Omega$	$1.8 \text{ m}\Omega$
r_{fb}	Internal resistance (discharging)	$1.9 \text{ m}\Omega$	$1.9 \text{ m}\Omega$

DDEs (4.10) and (4.11) are solved with Runge-Kutta fourth-order method [67, 75] for simulating the charging/discharging behavior. The time step is fixed at 0.1s. Memories are prepared to hold the values, which are used as the delay terms in DDEs (4.10) and (4.11). Here, $dI(t)/dt = 0$ and $I(t) = I$ because the current is fixed.

The following initial condition is set for the simulation.

$$\begin{cases} c_i(0) = c_0, \frac{dc_{\text{main}}(0)}{dt} = -\frac{I}{\alpha_c F}, \frac{dc_{\text{monitor}}(0)}{dt} = 0, \\ c_i(\tau_0) = c_0, \frac{dc_{\text{main}}(\tau_0)}{dt} = \frac{dc_{\text{monitor}}(\tau_0)}{dt} = 0. \end{cases} \quad (4.13)$$

Here, $\tau_0 \in [-\tau_d, 0)$. $dc_{\text{main}}(0)/dt$ includes the term derived from the redox reaction.

$dc_{\text{main}}(t)/dt$ is discontinuous at the moment of the current switching. The mass balance equation in each main cell (4.3) gives condition (4.14) to the left and the right-hand limits of $dc_{\text{main}}(t)/dt$ because the rate of reactant flow continuously changes.

$$\frac{dc_{\text{main}+}}{dt} + \frac{I_+}{\alpha_c F} = \frac{dc_{\text{main}-}}{dt} + \frac{I_-}{\alpha_c F} \quad (4.14)$$

Here, $dc_{\text{main}\pm}/dt = \lim_{t \rightarrow t_s \pm 0} dc_{\text{main}}(t)/dt$, $I_- = -50 \text{ A}$, and $I_+ = 50 \text{ A}$. $t = t_s$ is the time of switching, and $dc_{\text{main}}(t)/dt$ is switched under condition (4.14) at this moment.

The parameters for the model with transport delay are listed in Table 4.2. The flow rate at the inlet of the cell stack in Table 4.1 is divided by the number of

the cells, $m + 1$, and the quotient is given as W . The model has four fitting parameters; α_c , α_t , r_{rfb} , and τ_d . The method for fitting these parameters is explained in Appendix C.

Figure 4.5 shows the simulation result without transport delay ($\tau_d = 0$) and the result with the transport delay $\tau_d = 19.0$ s. The flow rate of the electrolyte in each cell is fixed at $W = 0.3 \text{ Lmin}^{-1}$. The simulation results are described by the lines, and the dots show the experimental data. As Figure 4.5(a) shows, the time delay in the mode switching appears in the simulation result without the transport delay. However, the length of the delay of the mode switching in the simulation is shorter than the experiment. Figure 4.5(b) reveals that that model precisely reproduces the charging time and the delay of the mode switching by accepting the transport delay. It is also found that the curve appears in $\Delta V(t)$ regardless of the transport delay, as Figures 4.5(c)–(f) show. The transfer of reactant in the cells is considered to appear as the $\Delta V(t)$ curve.

Figure 4.6 shows the effect of the flow rate of the electrolyte. The model precisely reproduces the experimental results by adjusting τ_d to 19 s for $W=0.3 \text{ Lmin}^{-1}$ and to 15.0 s for $W=0.5 \text{ Lmin}^{-1}$. τ_d depends on the flow rate of the electrolyte. It is natural because τ_d is derived from the transport time from the tank to the cells.

The volume of the electrolyte listed in Table 4.2 is smaller than the setting for the experimental setup in Table 4.1. Moreover, α_t depends on the flow rate of the electrolyte. The dead space is considered to appear in the tank and to result in the smaller value of α_t in the model.

4.2.3 Analysis of first-order lag in voltage

At the beginning of charging or discharging, $\Delta V(t)$ curves as the first-order lag response. The $\Delta V(t)$ is analyzed with an approximation. The approximation is introduced from the model with transport delay.

$\Delta V(t)$ contains the nonlinear function, $g(c_i)$, which is derived from Nernst equation.

$$\begin{aligned}\Delta V(t) &= V_{\text{main}}(t)/m - V_{\text{monitor}}(t) \\ &= g(c_{\text{main}}(t)) - r_{\text{rfb}}I - g(c_{\text{monitor}}(t))\end{aligned}\tag{4.15}$$

The nonlinear function can be linearized at the beginning of charging. The approx-

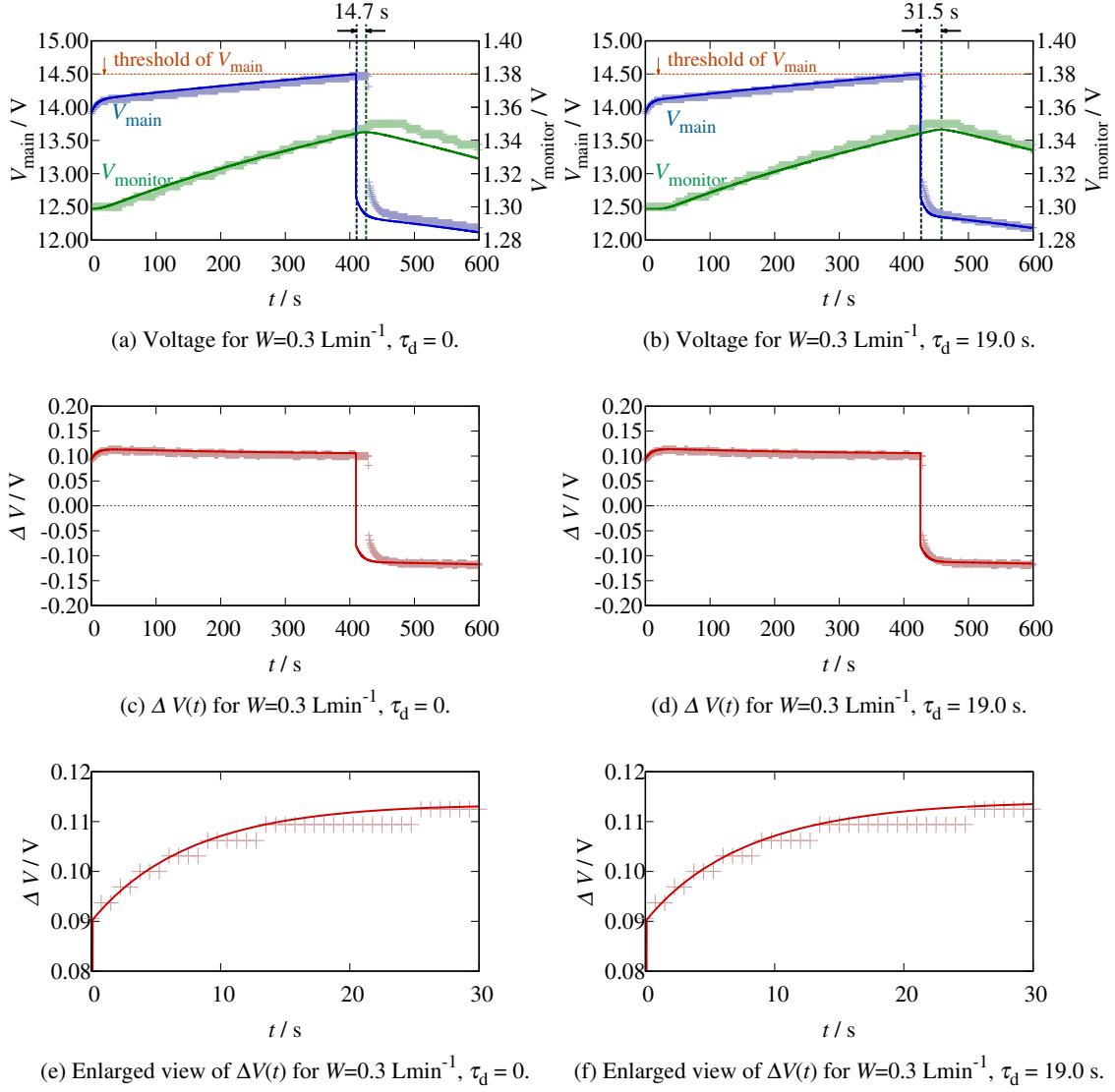


Figure 4.5: Dependence of simulation results on transport delay, τ_d . W refers to the flow rate of the electrolyte in each cell. The lines show the simulation results, and the dots are given from the experiment. (a), (b) Total voltage of main cells and voltage of monitor cell. (c), (d) Difference between averaged voltage of main cells and voltage of monitor cell ($\Delta V(t) = V_{\text{main}}(t)/m - V_{\text{monitor}}(t)$). (e), (f) Enlarged view of $\Delta V(t)$.

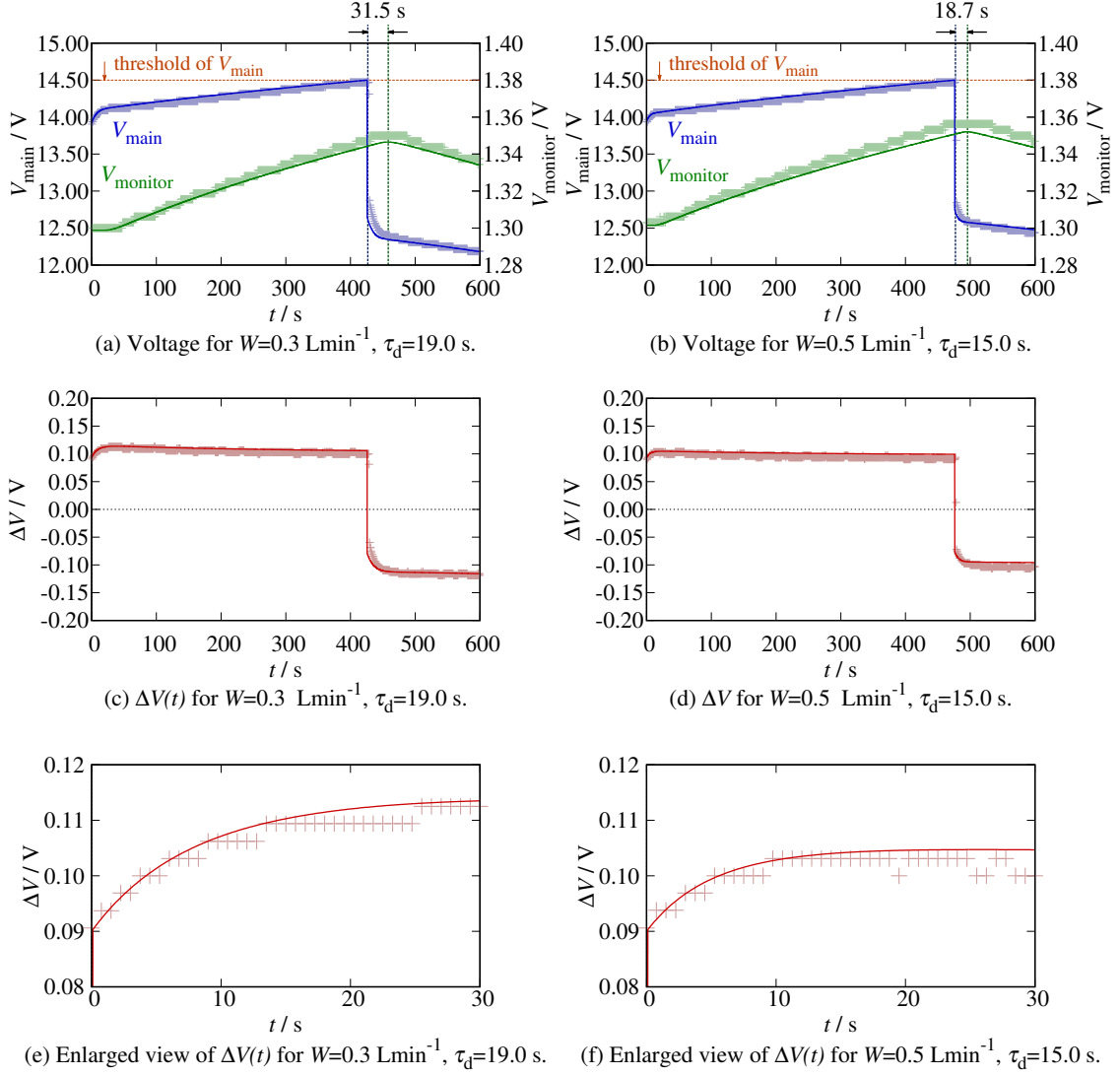


Figure 4.6: Dependence of simulation results and transport delay, τ_d , on flow rate of the electrolyte in each cell, W . The line shows the simulation results, and the dots are given from the experiment. (a), (b) Total voltage of main cells and voltage of monitor cell. (c), (d) Difference between averaged voltage of the main cells and voltage of the monitor cell ($\Delta V(t) = V_{\text{main}}(t)/m - V_{\text{monitor}}(t)$). (e), (f) Enlarged view of $\Delta V(t)$.

imation of $\Delta V(t)$ is given by linearizing $g(c_i)$ as following equation (4.16).

$$\Delta V(t) \approx g'(c_0 \Delta c(t)) - r_{\text{rfb}} I \quad (4.16)$$

Here, $\Delta c(t) = c_{\text{main}}(t) - c_{\text{monitor}}(t)$, and $c_0 = c_{\text{main}}(0) = c_{\text{monitor}}(0)$. Appendix D explains the detailed process for the linearization and evaluates the error.

$\Delta c(t)$ is given by ODE (4.17), which is obtained by taking the difference between DDEs (4.10) and (4.11).

$$\begin{aligned} \frac{d^2(\Delta c(t))}{dt^2} &= -\frac{W}{\alpha_c} \frac{d(\Delta c(t))}{dt} - \frac{1}{\alpha_c F} \frac{dI(t)}{dt} \\ &= -\frac{W}{\alpha_c} \frac{d(\Delta c(t))}{dt} \end{aligned} \quad (4.17)$$

ODE (4.17) does not include the transport delay, τ_d . The solution of ODE (4.17) is analytically obtained as follows.

$$\Delta c(t) = -\frac{I}{WF} \left(1 - e^{-\frac{t}{\tau_c}} \right), \quad \tau_c = \frac{\alpha_c}{W} \quad (4.18)$$

Analytic solution (4.18) implies that $\Delta c(t)$ approaches a constant value $\Delta c = -I/WF$ within the time constant $\tau_c = \alpha_c/W$. $\Delta V(t)$ is rescaled by τ_c .

$$\Delta V(t) = -g'(c_0) \frac{I}{WF} \left(1 - e^{-\frac{t}{\tau_c}} \right) - r_{\text{rfb}} I \quad (4.19)$$

Figure 4.7 verifies the dependence of τ_c on the flow rate of the electrolyte. The theoretically obtained τ_c is evaluated by the solid line. When approximation (4.19) fits $\Delta V(t)$ in the experimental data, τ_c is extracted as a parameter of approximation (4.19). The dots show the extracted value. The flow dependence of the extracted τ_c is similar to its theoretical prediction. τ_c is the time for the electrolyte to flow thorough each cell, and the similarity implies that the curve in $\Delta V(t)$ appears due to the transfer of the reactant in the cells.

4.3 Summary

This chapter proposed the charging/discharging model of RFBs with transport delay. The existence of the transport delay is indicated by the voltage of the monitor cell. The model precisely reproduces the voltage behavior in the experiment. The proposed model is physically reasonable both in the steady-state and in the transient state. The fitted parameter reflects the structure of the fluid circuit.

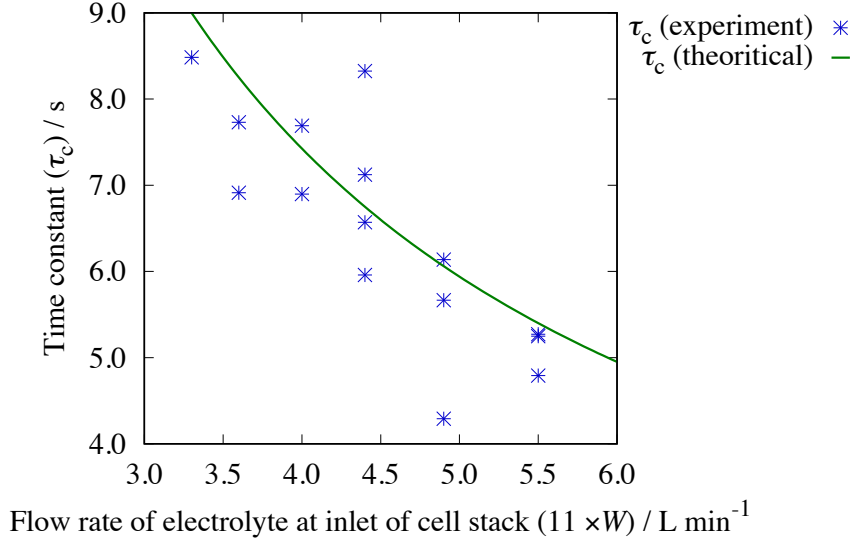


Figure 4.7: Flow dependence of time constant, τ_c . W is the flow rate of the electrolyte in each cell, and a_{11} is the number of the cells. The solid line is obtained by $\tau_c (= \alpha_c / W)$, where α_c is the volume of the electrolyte in each cell. α_c is set at 0.045 L in the simulation. The dots are extracted by fitting the approximation of $\Delta V(t)$ to the experimental data.

The model with transport delay has two contributions. One of the contributions is that the transport delay can be evaluated through the fitting. As mentioned above, the transport delay depends on the flow rate of the electrolyte. The dependence can be analyzed by parameter fitting of the model. The other contribution is that the charging/discharging can be simulated and analyzed with consideration for the transport delay. Chapter 5 employs the model introduced in this chapter for predicting the current-restriction in the proto-type RFB.

Chapter 5

Prediction of current-restriction by mass transport

Chapter 5 proposes the method for predicting the current-restriction by mass transport. The numerical study in Chapter 3 indicates that the current is eventually restricted by the mass transport from the tanks to the cells. If the current-restriction is predicted, it can be avoided by controlling the electrolyte flow. The prediction requires a model for simulating the discharging behavior and an indicator for extracting the current-restriction. The model with transport delay in Chapter 4 can be employed to simulate the discharging behavior. The previous researches [76,77] used the current determined by the rate of diffusion for extracting the current-restriction by diffusion. The rate of diffusion depends on the flow rate of the electrolytes and the SOC, and it is difficult to verify the rate of diffusion in the operations. As an alternative to the rate of diffusion, this chapter calculates the current from the rate of the mass transport from the tanks to the cells, and calls the current “limited-current.” The flow rate of the electrolyte determines the rate of mass transport, and it can be easily measured. Section 5.1 introduces the limited-current. Section 5.2 shows the prediction of the current-restriction in the simulation. Section 5.3 verifies that the proto-type RFB is restricted by the mass transport in the experiment, as predicted in the simulation.

5.1 Introduction of limited-current

This section introduces the limited-current, which indicates the restriction of the current by the mass transport from the tanks to the cells. The limited-current is introduced based on the reaction process in the negative half cells.

Let v_{r-} be the rate of discharging reaction in the negative half cells. Faraday's law [64] gives the following relationship between the rate of discharging reaction and the discharging current.

$$I(t) = \alpha_c F v_{r-} \quad (5.1)$$

Here, α_c is the volume of the electrolyte in each negative half cell, and F is Faraday constant.

The following equation (5.2) gives the flow rate of V^+ at the inlet of the negative half cell.

$$v_{f-}(t) = \frac{W}{\alpha_c} [V^{2+}]_{\text{tank}}(t - \tau_d) \quad (5.2)$$

The transport time from the tank to the cells is taken into account here, and $[V^{2+}]_{\text{tank}}(t - \tau_d)$ represents the concentration of V^{2+} in the negative tank at $t = t - \tau_d$. W is the flow rate of the electrolyte.

Suppose that most of V^+ in the negative half cell has already been consumed due to the high current and the fast discharging reaction. The rate of the discharging reaction v_{r-} is balanced with the flow rate of reactant, v_{f-} .

$$v_{r-}(t) = v_{f-}(t) \quad (5.3)$$

The limited-current, I_{lim} , is given by the combination of equations (5.1)–(5.3).

$$I_{\text{lim}}(t) = FW[V^{2+}]_{\text{tank}}(t - \tau_d) \quad (5.4)$$

The limited-current can also be introduced from the discharging reaction in the positive half cells by proceeding along with the introduction from the negative half cells. The limited-current can be rewritten due to the symmetry between the negative and the positive half cells, as follows.

$$I_{\text{lim}}(t) = FW[V^{2+}]_{\text{tank}}(t - \tau_d) = FWc_{\text{tank}}(t - \tau_d) \quad (5.5)$$

$c_{\text{tank}}(t)$ is the reactant concentration in the tank. The current coincides with the limited-current when the mass transport restricts the discharging current.

The reactant concentration in the tank, $c_{\text{tank}}(t)$, is needed for calculating I_{lim} . $c_{\text{tank}}(t)$ is simulated by solving the differential equation (4.9) of $c_{\text{tank}}(t)$ in Chapter 4.

5.2 Prediction of current-restriction in simulation

The proto-type RFB modeled in Chapter 4 is integrated into a 300 A class discharging circuit. The restriction by the mass transport is predicted by the limited-current and the model with transport delay.

5.2.1 Simulation setup

Suppose that the RFB is integrated into the discharging circuit described in Figure 5.1. L denotes a parasitic inductance. Every load resistance, r_{load} , is connected to a MOSFET in series. The number of load resistances is discontinuously changed by switching with the MOSFETs. The MOSFETs are assumed to switch instantly.

Kirchhoff's voltage law gives the current change in the discharging circuit by equation (5.6).

$$\begin{aligned} \frac{dI(t)}{dt} &= -\frac{1}{L} \left\{ \left(\frac{r_{\text{load}}}{n(t)} \right) I(t) - V_{\text{main}}(t) \right\} \\ &= -\frac{1}{L} \left\{ \left(\frac{r_{\text{load}}}{n(t)} - mr_{\text{rfb}} \right) I(t) - m \left(E_{\text{eh}}^0 + \frac{2RT}{F} \ln \frac{c_{\text{main}}(t)}{c_{\text{max}} - c_{\text{main}}(t)} \right) \right\} \end{aligned} \quad (5.6)$$

$n(t)$ denotes the number of load resistances connected to the RFB.

The number of connected resistances, n , changes under the following two modes.

(a1) Constant load mode;

$$n(t) = 4, t \geq 0 \quad (5.7)$$

(a2) Periodic load variation mode;

$$n(t) = \begin{cases} 4 & \left(k\Delta t \leq t < \frac{2k+1}{2}\Delta t \right) \\ 1 & \left(\frac{2k+1}{2}\Delta t \leq t < (k+1)\Delta t \right) \end{cases} \quad (5.8)$$

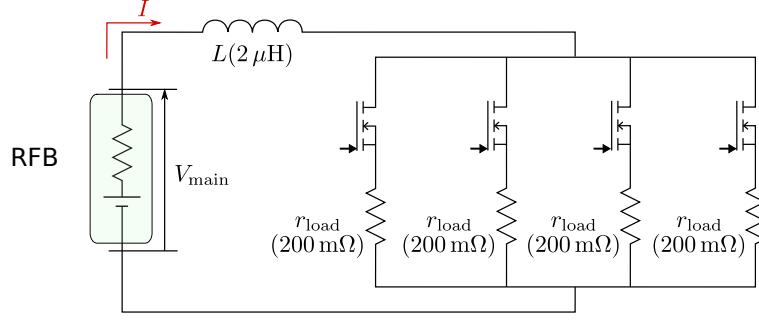


Figure 5.1: Discharging circuit integrating proto-type RFB. Every load resistance, r_{load} , is connected to a MOSFET in series. The number of resistances connected to the proto-type RFB changes by MOSFET switching, which represents the load variation. I is the discharging current, and V_{main} is the total voltage of the main cells.

Here, $k \in \mathbb{Z}$, $k \geq 0$, and Δt is the period of load variation.

c_i ($i = \text{main, monitor}$) is simulated by solving the following differential equations, which are given by substituting ODE (5.6) into DDEs (4.10) and (4.11) in the model with transport delay.

$$\begin{aligned} \frac{d^2 c_{\text{main}}(t)}{dt^2} = & -\frac{W}{\alpha_c} \frac{dc_{\text{main}}(t)}{dt} - \frac{mW}{\alpha_t} \frac{dc_{\text{main}}(t - \tau_d)}{dt} - \frac{W}{\alpha_t} \frac{dc_{\text{monitor}}(t - \tau_d)}{dt} \\ & - \frac{mWI(t - \tau_d)}{\alpha_c \alpha_t F} + \frac{1}{\alpha_c FL} \left(\frac{r_{\text{load}}}{n(t)} - mr_{\text{rfb}} \right) I(t) \\ & - \frac{m}{\alpha_c FL} \left(E_{\text{eh}}^0 + \frac{2RT}{F} \ln \frac{c_{\text{main}}(t)}{c_{\text{max}} - c_{\text{main}}(t)} \right) \end{aligned} \quad (5.9)$$

$$\begin{aligned} \frac{d^2 c_{\text{monitor}}(t)}{dt^2} = & -\frac{W}{\alpha_c} \frac{dc_{\text{monitor}}(t)}{dt} - \frac{mW}{\alpha_t} \frac{dc_{\text{main}}(t - \tau_d)}{dt} \\ & - \frac{W}{\alpha_t} \frac{dc_{\text{monitor}}(t - \tau_d)}{dt} - \frac{mWI(t - \tau_d)}{\alpha_c \alpha_t F} \end{aligned} \quad (5.10)$$

The discharging behavior is simulated by solving differential equations (5.6), (5.9), and (5.10). The initial condition is set as follows.

$$\begin{cases} c_{\text{main}}(t_0) = c_{\text{monitor}}(t_0) = c_{\text{tank}}(t_0) = 0.8 \text{ molL}^{-1}, \\ \frac{dc_{\text{main}}(t_0)}{dt} = \frac{dc_{\text{monitor}}(t_0)}{dt} = \frac{dc_{\text{tank}}(t_0)}{dt} = 0, \\ I(t_0) = 0 \end{cases} \quad (5.11)$$

Table 5.1: Parameter setting for model of RFB.

Symbol	Name	Value
m	Number of cells	10
W	Flow rate of electrolyte in each cell	0.6 Lmin^{-1}
α_t	Volume of electrolyte in each tank	7.31 L
α_c	Volume of electrolyte in each half cell	40 mL
r_{rfb}	Internal resistance of each cell	$2.1 \text{ m}\Omega$
T	Temperature	305 K
τ_d	Transport delay	19.0 s

Here, $t \in [-\tau_d, 0]$. The RFB has no load for $t < 0$. The fourth-order Runge–Kutta method [67,75] was applied for the simulation. The step size is fixed at 10^{-5} s. The reactant concentration should be positive, and the finishing condition is given as follows.

$$(c_{\text{main}}(t) \leq 0) \cup (c_{\text{monitor}}(t) \leq 0) \cup (c_{\text{tank}}(t) \leq 0) \quad (5.12)$$

The parameters of the RFB are listed in Table 5.1.

5.2.2 Simulation result

This subsection shows the prediction of the current-restriction. Figure 5.2 shows the discharging behavior for constant load mode (5.7), and Figure 5.3 shows for periodic load mode (5.8).

The discharging behavior for constant load mode (5.7) is restricted by the mass transport around $t = 300$ s. The discharging current approaches to the limited-current and decreases quickly. The order of c_{main} is smaller than $10^{-3} \text{ molL}^{-1}$ in this term. The simulation stops around $t = 350$ s after satisfying finishing condition (5.12).

The restriction appears around $t = 400$ s and after $t = 480$ s for periodic load variation mode (5.8). Δt is set to 120 s. The current coincides with the limited-

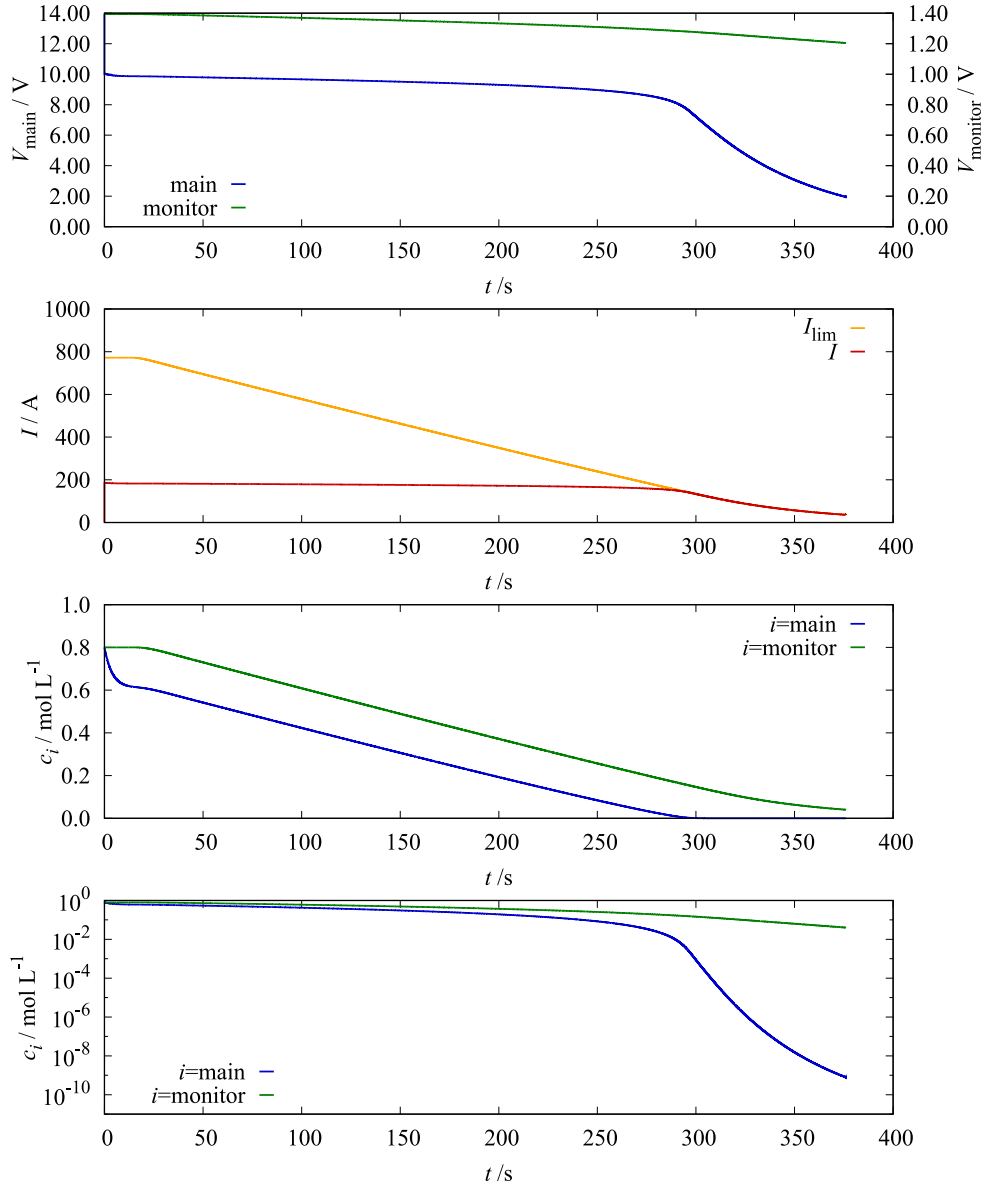


Figure 5.2: Simulation results for constant load mode. The number of load resistances is fixed at $n = 4$.

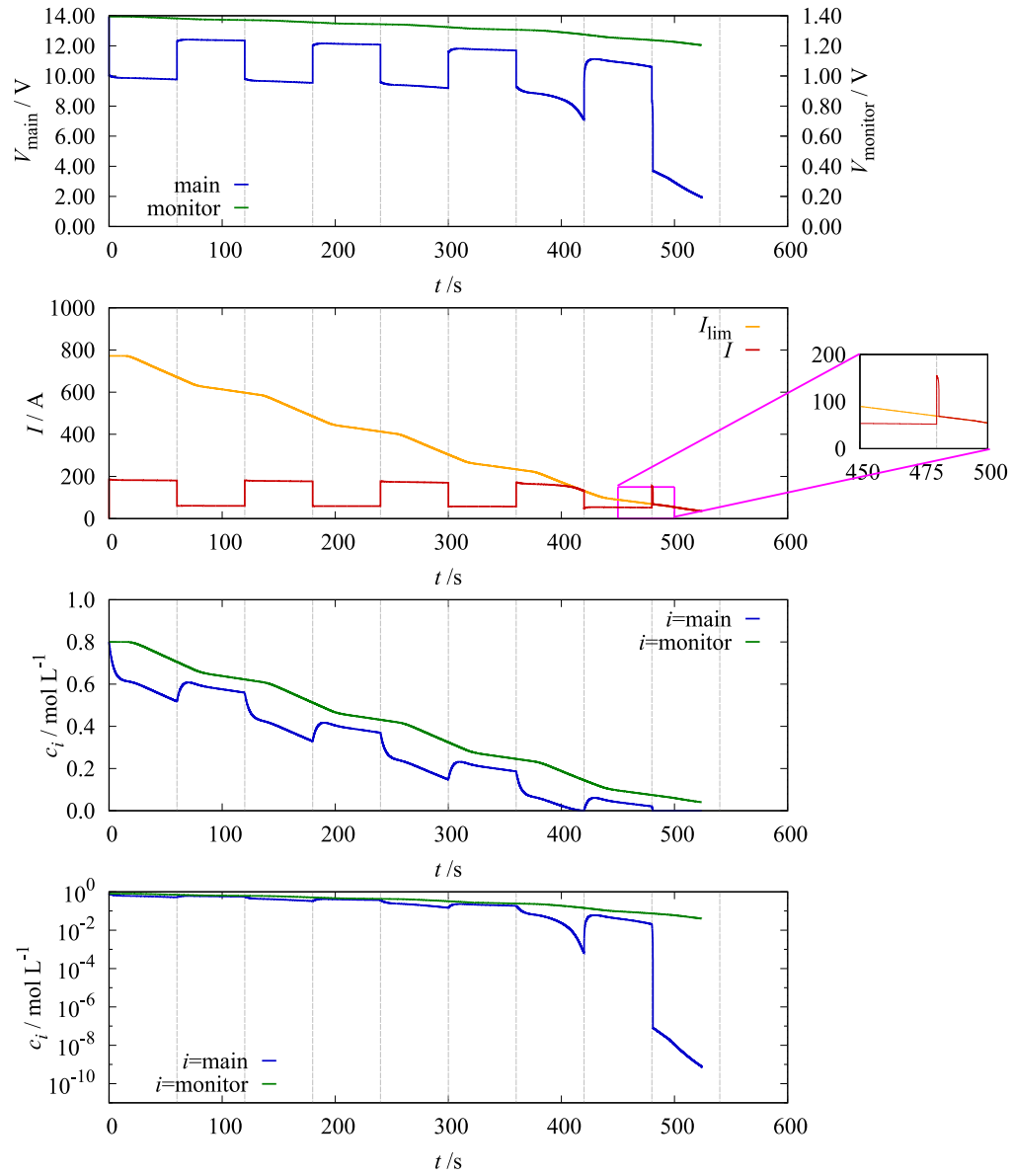


Figure 5.3: Simulation results for periodic load variation mode. The number of load resistances, n , changes periodically between $n = 1$ and $n = 4$. The period is 120 s.

current around $t = 400$ s and exceeds the limited-current after the switching at $t = 480$ s. The temporary increase of $I(t)$ is considered to be caused by the increase of $c_{\text{main}}(t)$. The supply rate of reactant is faster than the consumption due to the discharging reaction after the switching at $t = 420$ s. Therefore, $c_{\text{main}}(t)$ temporally increases, and the condition for the mass transport to restrict the current is not satisfied in this short period. The replenished reactant is instantly consumed due to the sudden increase of the current at $t = 480$ s, and the current is restricted by the mass transport again.

The change rate of reactant concentration, $dc_i(t)/dt$, can be associated with the current-restriction. $dc_i(t)/dt$ converges to the following value for $I(t) \ll I_{\text{lim}}(t)$ in Figure 5.4

$$\frac{dc_i(t)}{dt} \rightarrow -\frac{mI(t - \tau_d)}{((m + 1)\alpha_c + \alpha_t)F} = f(I(t - \tau_d)) \quad (5.13)$$

If $I(t) \approx I_{\text{lim}}(t)$, $dc_{\text{main}}(t)/dt$ does not approach the line referring to $f(I(t - \tau_d))$. The approach of $dc_{\text{main}}(t)/dt$ to 0 can be clearly explained by following mass balance equation in each main cell.

$$\frac{dc_{\text{main}}(t)}{dt} = -\frac{I(t)}{\alpha_c F} + \frac{W}{\alpha_c}(c_{\text{tank}}(t - \tau_d) - c_{\text{main}}(t)) \quad (5.14)$$

$$\approx -\frac{I_{\text{lim}}(t)}{\alpha_c F} + \frac{W}{\alpha_c}c_{\text{tank}}(t - \tau_d) = 0 \quad (5.15)$$

Here, $c_{\text{main}}(t) \approx 0$ and $I(t) = I_{\text{lim}}(t)$.

5.3 Verification of prediction in experiment

This section verifies the prediction in Section 5.2 by comparing the simulated current to the current in the experiment. The discharging circuit in Figure 5.1 is implemented for the experiment and connected to the proto-type RFB.

5.3.1 Experimental setup

Figure 5.5 shows the photograph of the proto-type RFB and the 300 A class discharging circuit. The circuit consists of the output port of the proto-type RFB, load resistances, Si MOSFETs (IXFN, IXFN420N10T), and additional capacitors

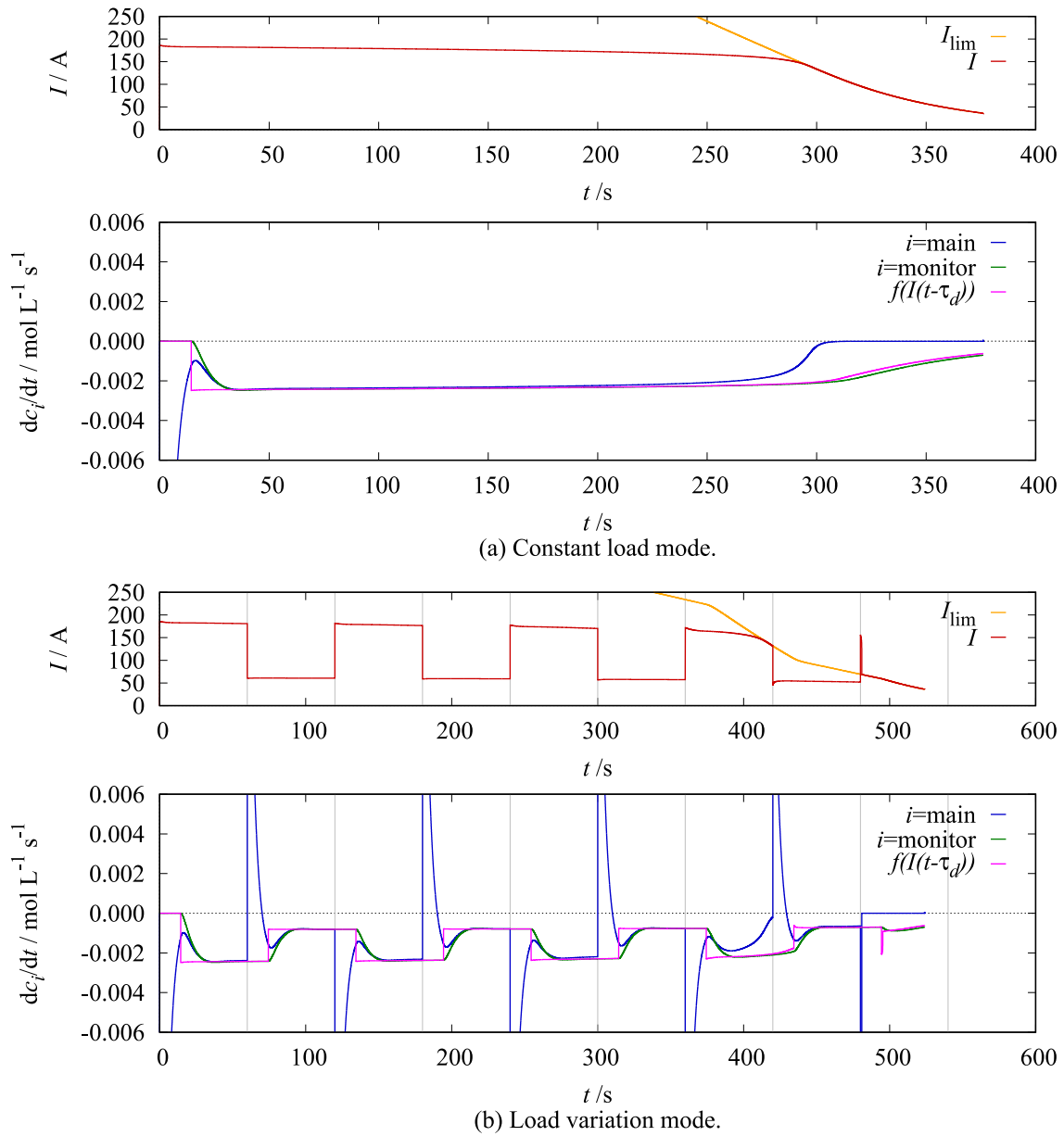


Figure 5.4: Change rate of reactant concentration. $dc_i(t)/dt = f(I(t - \tau_d))$ refers to the steady-state for $I(t) \ll I_{\text{lim}}(t)$. (a) Constant load mode. (b) Periodic load variation mode, the number of load changes periodically between $n = 1$ and $n = 4$. The period is 120 s.

of $100\ \mu\text{F}$. Each capacitor is connected in parallel with a MOSFET for suppressing the surge voltages. The rated power of each load resistance ($200\ \text{m}\Omega$) is $800\ \text{W}$.

Each MOSFET is driven by a gate driver (Silicon Labs, Si8235BB-C-IS1). The input signals to the gate drivers are generated by a controller board (National Instruments, sbRIO 9607). For protection, the output port of the controller is isolated from the input port of the gate driver.

The state of MOSFETs, S_l ($l = 1, 2, 3, 4$), switches according to the following load modes.

(a1) For the constant load mode:

$$S_l = \text{ON}, \quad l = 1, 2, 3, 4 \quad (t \geq 0) \quad (5.16)$$

(a2) For the periodic load variation mode:

$$S_1 = S_2 = S_3 = \begin{cases} \text{ON} & \left(k\Delta t \leq t < \frac{2k+1}{2}\Delta t \right) \\ \text{OFF} & \left(\frac{2k+1}{2}\Delta t \leq t < (k+1)\Delta t \right) \end{cases} \quad (5.17)$$

$$S_4 = \text{ON} \quad (t \geq 0)$$

The voltage and the current are measured with a current transducer (LEM, HTA 400-S) and a memory hicoder (HIOKI, 4081). The value of the current was converted into a voltage signal with the current transducer. The memory hicoder stores the converted voltage signal, the total voltage of the main cells, V_{main} , and the EMF of the monitor cell, V_{monitor} .

5.3.2 Comparison of simulation and experiment

This subsection compares the experimental results with the simulation results. The reactant was distributed uniformly in the RFB before discharging. The main cells were not connected to the discharging circuit in $t < 0$, and all MOSFETs were activated at $t = 0$.

The experimental results are compared to the simulation results in Figure 5.6. The proto-type RFB shows similar behaviors to the simulation results. The current drops rapidly around $t = 300\ \text{s}$ in the constant load mode, as shown in Figure 5.6(a). In addition, Figure 5.6(b) shows that the current is restricted after the temporary increase of the current in the proto-type RFB, being consistent with the simulation.

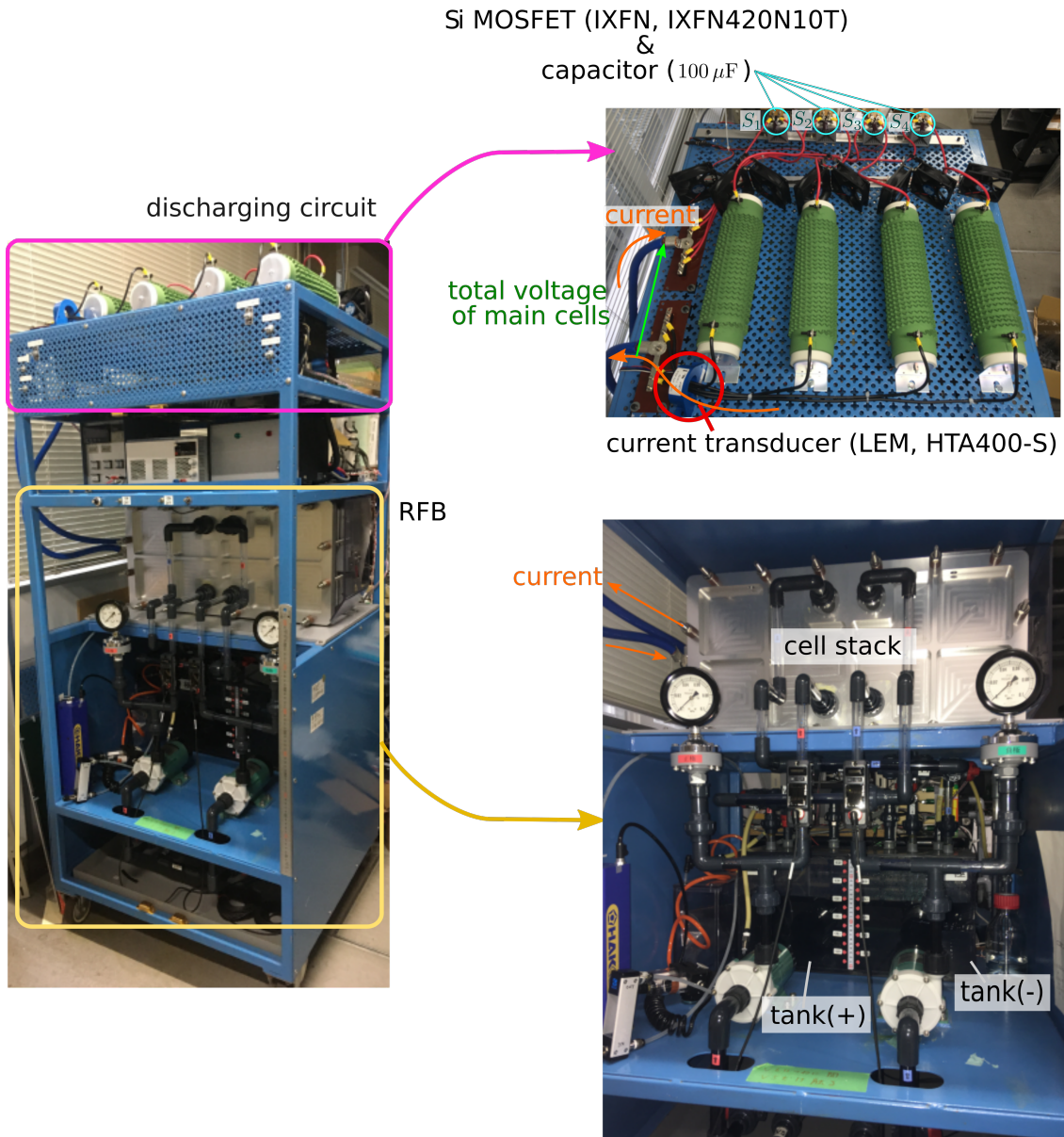
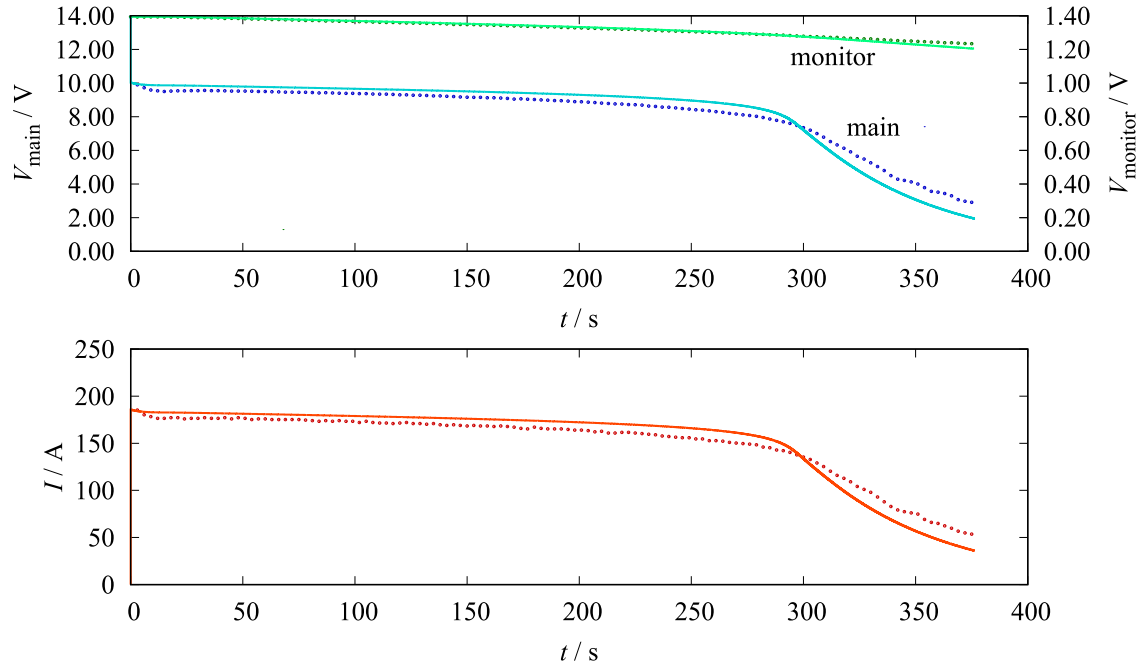
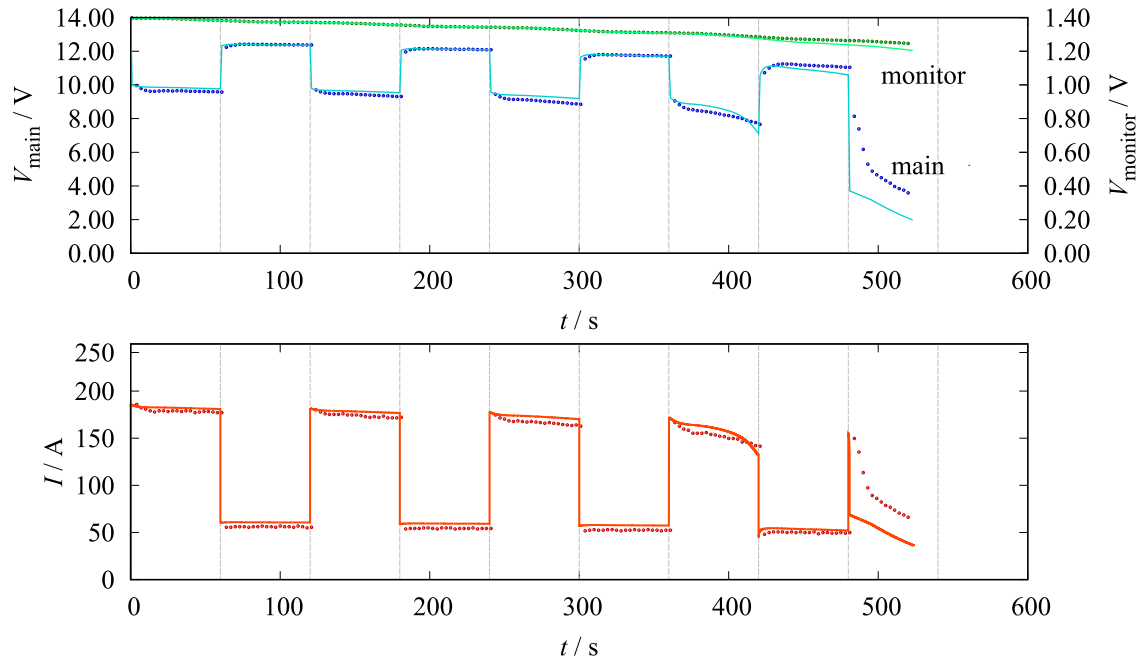


Figure 5.5: Photograph of experimental setup. This system consists of a proto-type RFB and a discharging circuit. The state of MOSFETs, S_l ($l = 1, 2, 3, 4$), changes according to the signal generated by a controller.



(a) Constant load mode.



(b) Load variation mode.

Figure 5.6: Comparison between experimental and simulation results. The dots show the experimental results, and the solid line shows the simulation results. The number of load resistances, n , changes periodically between $n = 1$ and $n = 4$. The period is 120 s.

The proto-type RFB in the experiment discharges at a slower rate with the comparison to the model in the simulation. The rate of discharge is mainly determined by the load current for $I \ll I_{\text{lim}}$, as explained by equation (5.13). The current measured in the experiment is smaller than that in the simulation. The difference in the current is considered to result in the slow discharge in the experiment.

The difference in the current indicates that the internal resistance of the cells changes according to the current. The current in the simulation coincides with the experiment at $t = 0$ in Figure 5.6(a) and at the switching from $n = 1$ to $n = 4$ in Figure 5.6(b). The resistance listed in Table 5.1 is valid at these instants. However, the current changes transiently, and the value in the experiment becomes smaller than the simulation. The transient behavior appears for the high current, and cannot be precisely reproduced by assuming the constant internal resistance.

The change in the internal resistance may be derived from the concentration overpotential [50]. The reactant in the cells is assumed to distribute uniformly in Chapter 2. The overpotential is approximated as $\eta_{\pm} = r_{\pm}I$ based on this assumption. However, the reactant in the neighborhood of the electrode is consumed rapidly for the high current, and the gradient of the reactant concentration is not negligible. If the term derived from the gradient of the reactant concentration is dominant in the overpotential given by Butler-Volmer equation (2.9), the overpotential in the negative half cell is approximated as equation (5.18) [50, 64].

$$\eta_- = \frac{RT}{\alpha F} \ln \frac{c_2^b}{c_2^s} \quad (5.18)$$

Here, the overpotential increases depending on the gradient of the reactant concentration, and the internal resistance increases with the gradient of the reactant concentration. The overpotential in the positive half cell is also approximated in the same way as equation (5.18). The researches of the high power RFB systems [78, 79] are discussing the effect of the concentration overpotential and trying to reduce it.

5.4 Summary

The prediction method proposed in this chapter enables to confirm whether the RFBs can supply the requested power under load variations. The discharging current is simulated by the model with transport delay, and the limited-current works as the indicator of the current-restriction. The current in the experiment is restricted

by the mass transport, as predicted in the simulation. The current-restriction in the experiment appears after than that in the simulation because of the fast rate of discharge. The ability of the proto-type RFB as the power supply is secured in the time domain, in which the RFB in the simulation discharges without the restriction. The difference in the rate of discharge is not critical for confirming the ability of the RFBs in the circuit under the load variations.

The proposed prediction method has the potential to contribute to avoid the current-restriction by the mass transport. The mass transport depends on the flow rate of the electrolyte. The current-restriction can be avoided by controlling the electrolyte flow based on the prediction of the current-restriction if the accuracy of the prediction is improved.

Chapter 6

Conclusion and future directions

6.1 Conclusion

This dissertation aimed to give the direction for designing the flow control system, which enables RFBs to supply power without the restriction by mass transport. For this purpose, the discharging behavior of the cells were simulated and analyzed. The focus was given to the effect of mass transport from the tanks to the cells. The flow rate of the electrolytes and the transport time were picked as the parameters which reflect the effect of mass transport.

Chapter 2 explained the assumptions on redox reactions and mass transport in RFBs and introduced the fundamental equations for modeling. The charging/discharging of the cells was defined as the increase/decrease of the reactant (V^{2+} or VO_2^+) in the cells. The EMF and the output voltage were associated with the reactant concentration. In addition, the mass balance equations were introduced as the basis for describing the charging/discharging behavior with the differential equations.

Chapter 3 described the simulation results of the discharging behavior of the micro RFB in the circuit, which was short-circuited. In the simulation, the focus was on the flow rate of the electrolyte, and the transport time was assumed to be negligible. The simulation results revealed that discharging behavior varied according to the flow rate of the electrolyte. The discharging behaviors were categorized into three cases. For the slow rate of the electrolyte flow, the reactant in the cell is depleted, and the discharging stopped without consuming the reactant in the tank. In this case, the voltage and the current dropped rapidly, and the power supply

stopped. For the fast rate of the electrolyte flow, the reactant in the tank were consumed, and the oscillation did not occur. However, the current eventually seemed to be restricted by the mass transport from the tanks to the cell. In addition to these cases, the oscillation occurred in the current, the voltage, and the reactant concentration in the cell for some flow conditions. The difference in three types of discharging behavior appeared in approaching the state in which the current was restricted by the mass transport from the tank to the cell. The simulation results revealed the discharging behavior for low reactant concentration and the underlying dynamics.

Chapter 4 introduced the charging/discharging model with a transport delay for simulating the behavior of the large scale RFB systems. The model was developed from the mass balance equations, which assume the finite single transport delay. The charging/discharging dynamics were described by DDEs. The model precisely simulated the voltage behavior of the proto-type RFB system, which was significantly affected by transport delay. The charging/discharging behavior can be simulated and analyzed with consideration for the transport delay.

Chapter 5 proposed the method for predicting the current-restriction by the mass transport from the tank to the cells. The limited-current was introduced for extracting the current-restriction. The limited-current was calculated from the rate of the mass transport from the tank to the cell. The current-restriction was predicted by comparing the limited-current to the discharging current. The discharging current was estimated by the model with transport delay in Chapter 4. The proto-type RFB verified that the current was restricted by mass transport, as predicted by the proposed method. The system for avoiding the current-restriction can be designed based on the prediction with the proposed method.

6.2 Future directions

The discussion in this dissertation gives some directions to control the electrolyte flow in RFBs. As mentioned in Chapter 3, the voltage and the current drops rapidly due to the depletion of the reactant. The dynamics of the fluid system is slow in comparison with the electrical behavior. The flow control system will fail to avoid the drop in the voltage and the current of RFBs if the electrolyte flow is pumped up after the detection. This electrical behavior indicates that the electrolytes should be

pumped up dynamically based on the prediction. Feed-forward approach is required for maintaining the output power of the RFBs. The current-restriction is predicted with the method proposed in Chapter 5. The optimized flow rate of the electrolytes can be selected based on the prediction for avoiding the current-restriction.

The prediction with the model leaves the problem in the accuracy for high current. The error is considered to appear due to the increase of the loss derived from the distribution of reactants in the cells. The loss is called concentration overpotential, and the study of the concentration overpotential will help the improvement of the overall accuracy. The flow control system with the accurate model will support the power supply with RFBs and help the grid balancing.

RFBs has the potential to enlarge its application by taking the flexible fluid network [80–82]. The report [80] shows the use of the RFB as the DC-DC transformer. The multiple cell-stacks are integrated into the circulation system of the electrolytes, and each stack is connected to the different loads or sources. The voltage of the load is adjusted by the number of cells in the stack. The papers [81,82] suggests the addition of the reactors to the circulation system of the electrolytes for producing hydrogen and oxygen. These gases are supplied to FCs. The cell stacks and the reactors become the node of the fluid network, and the pipes are the edges. Of course, mass transport between the nodes is a critical factor in this network.

The discussion in this dissertation can be extended to design the fluid network consisting of multiple cell stack. This system can be described as a coupled system, and the model will be introduced from almost the same assumptions in Chapter 2. The transport delay is negligible if the spatial scale of the fluid network is small. The coupling coefficient becomes large, and it can lead to the resonance. The analysis, like Chapter 3 will be required to clarify the dynamics in the small fluid network. For the large fluid network, the connection between the nodes becomes weak, but the transport delay cannot be neglected. This dissertation will also become the basis for designing RFB systems with the multiple-stack. RFB systems with the multiple-stack will get a new function and support the power grid in a way that cannot be exchanged by other types of batteries.

Appendix A

Introduction of dimensionless state equation

This chapter explains the introduction process of dimensionless state equation (3.9) in detail. As mentioned in Chapter 3, the variables c , dc/dt , I , and t are normalized to x_1 , x_2 , x_3 , and τ by using the constants $\hat{c}$, $\hat{t}$, and $\hat{I}$. Equations (A.1) and (A.2) are given by substituting x_1 , x_2 , x_3 , and τ in equation (3.7) to ODEs (3.2) and (3.3).

$$\frac{\hat{c}}{\hat{t}^2} \frac{dx_2}{d\tau} = -W \left(\frac{1}{\alpha_c} + \frac{1}{\alpha_t} \right) \frac{\hat{c}}{\hat{t}} x_2 + \left(\frac{r + r_{\text{rfb}}}{L} - \frac{W}{\alpha_t} \right) \frac{\hat{I}}{\alpha_c F} x_3 - \frac{1}{\alpha_c F L} \left(E_{\text{eh}}^0 + \frac{2RT}{F} \ln \frac{\hat{c} x_1}{c_{\text{max}} - \hat{c} x_1} \right) \quad (\text{A.1})$$

$$\frac{\hat{I}}{\hat{t}} \frac{dx_3}{d\tau} = -\frac{1}{L} \left\{ (r + r_{\text{rfb}}) \hat{I} x_3 - \left(E_{\text{eh}}^0 + \frac{2RT}{F} \ln \frac{\hat{c} x_1}{c_{\text{max}} - \hat{c} x_1} \right) \right\} \quad (\text{A.2})$$

Equation (A.1) is rewritten to equation (A.3) by multiplying equation (A.1) with $\hat{t}^2/\hat{c}$.

$$\frac{dx_2}{d\tau} = -W \left(\frac{1}{\alpha_c} + \frac{1}{\alpha_t} \right) \hat{t} x_2 + \left(\frac{r + r_{\text{rfb}}}{L} - \frac{W}{\alpha_t} \right) \frac{1}{\alpha_c F} \frac{\hat{I} \hat{t}^2}{\hat{c}} x_3 - \frac{1}{\alpha_c F L} \frac{\hat{t}^2}{\hat{c}} \left(E_{\text{eh}}^0 + \frac{2RT}{F} \ln \frac{x_1}{c_{\text{max}}/\hat{c} - x_1} \right) \quad (\text{A.3})$$

Suppose that the left hand of equation (A.3) is balanced with the terms derived from the electrical circuit. Here, following relationship (A.4) is given.

$$\frac{\hat{c}}{\hat{t}^2} = \frac{E_{\text{eh}}^0}{\alpha_c F L}, \quad \hat{I} = \frac{E_{\text{eh}}^0}{r + r_{\text{rfb}}} \quad (\text{A.4})$$

Equation (A.3) is rewritten to equation (A.5) due to relationship (A.4).

$$\begin{aligned} \frac{dx_2}{d\tau} &= -W \left(\frac{1}{\alpha_c} + \frac{1}{\alpha_t} \right) \hat{t} x_2 + \left(1 - \frac{WL}{\alpha_t(r + r_{\text{rfb}})} \right) x_3 \\ &\quad - \left(1 + \frac{2RT}{FE_{\text{eh}}^0} \ln \frac{\hat{c}x_1}{c_{\text{max}}/\hat{c} - \hat{c}x_1} \right) \\ &= -\beta x_2 + (1 - \gamma) x_3 - \left(1 + \delta \ln \frac{x_1}{1 - x_1} \right) \end{aligned} \quad (\text{A.5})$$

Here, β , γ , δ , $\hat{c}$ are given by equation (A.6).

$$\beta = W \left(\frac{1}{\alpha_c} + \frac{1}{\alpha_t} \right) \hat{t}, \quad \gamma = \frac{WL}{\alpha_t(r + r_{\text{rfb}})}, \quad \delta = \frac{2RT}{FE_{\text{eh}}^0}, \quad \hat{c} = c_{\text{max}} \quad (\text{A.6})$$

Equation (A.7) is given by multiplying equation (A.2) with $L/\hat{I}(r + r_{\text{rfb}})$.

$$\begin{aligned} \frac{L}{r + r_{\text{rfb}}} \frac{1}{\hat{t}} \frac{dx_3}{d\tau} &= -x_3 + \frac{1}{(r + r_{\text{rfb}})\hat{I}} \left(E_{\text{eh}}^0 + \frac{2RT}{F} \frac{\hat{c}x_1}{c_{\text{max}} - \hat{c}x_1} \right) \\ \Leftrightarrow \varepsilon \frac{dx_3}{d\tau} &= -x_3 + \left(1 + \delta \ln \frac{x_1}{1 - x_1} \right) \end{aligned} \quad (\text{A.7})$$

Here, ε implies the ratio of the time scales of the electrical circuit to the RFB. ε is given by equation (A.8).

$$\varepsilon = \frac{\hat{t}'}{\hat{t}}, \quad \hat{t}' = \frac{L}{r + r_{\text{rfb}}} \quad (\text{A.8})$$

Appendix B

Estimation of SOC with monitor cell

This chapter explains the method for estimating the SOC of the main cells from the voltage of the monitor cell. This method uses the inverse function of $g(c_i)$ ($i = \text{main, monitor}$).

The voltage of the main cells and the monitor cell are given by equations (B.1) and (B.2).

$$\begin{aligned} V_{\text{main}}(t) &= m\{g(c_{\text{main}}(t)) - r_{\text{rfb}}I(t)\} \\ &= m\left(E_{\text{eh}}^0 + \frac{2RT}{F} \ln \frac{c_{\text{monitor}}(t)}{c_{\text{max}} - c_{\text{monitor}}(t)} - r_{\text{rfb}}I(t)\right) \end{aligned} \quad (\text{B.1})$$

$$V_{\text{monitor}}(t) = g(c_{\text{monitor}}(t)) = E_{\text{eh}}^0 + \frac{2RT}{F} \ln \frac{c_{\text{monitor}}(t)}{c_{\text{max}} - c_{\text{monitor}}(t)} \quad (\text{B.2})$$

The voltage of the main cells includes the loss derived from the internal resistance, and the EMF cannot be measured directly.

Here is introduced critical condition (B.3) for estimating the SOC of the main cells through the EMF of the monitor cell.

$$\begin{aligned} c_{\text{main}} &\in \mathbb{A}, \\ \mathbb{A} &= \{c_{\text{main}} \in (0, c_{\text{max}}) \mid |g(c_{\text{main}}) - g(c_{\text{monitor}})| < \varepsilon_e\} \end{aligned} \quad (\text{B.3})$$

Condition (B.3) assures that the difference of the reactant concentration between the main and monitor cells is small enough to neglect the difference in the EMF of the cells.

Condition (B.3) requires the following conditions

- The supply of reactant to the main cells is sufficiently rapid compared to the rate of the redox reaction in the main cells.
- Reactant stored in the tanks instantly move to the cells via the pipes.

These conditions are satisfied under the fast rate of mass transport. Condition (B.3) gives the following relationship between the main cells and the monitor cell.

$$\begin{aligned} V_{\text{monitor}}(t) &= g(c_{\text{monitor}}(t)) \\ &\approx g(c_{\text{main}}(t)) \end{aligned} \quad (\text{B.4})$$

The function $g(c_i)$ is invertible. The reactant concentration and the SOC of the main cells can be estimated from the voltage of the monitor cell with the following equation (B.6).

$$c_{\text{main}}(t) \approx g^{-1}(V_{\text{monitor}}(t)) = \frac{c_{\text{max}}}{1 - \exp \left\{ \frac{2RT}{F(V_{\text{monitor}} - E_{\text{eh}}^0)} \right\}} \quad (\text{B.5})$$

$$\text{SOC} \approx \frac{1}{1 - \exp \left\{ \frac{2RT}{F(V_{\text{monitor}} - E_{\text{eh}}^0)} \right\}} \quad (\text{B.6})$$

Appendix C

Parameter fitting of model with transport delay

The model with transport delay has four fitting parameters; α_c , α_t , r_{rfb} and τ_d . α_c and α_t refer to the volume of the electrolytes in each cell and each tank. r_{rfb} is the internal resistance. τ_d is the transport time.

r_{rfb} is extracted from the difference between the averaged voltage of the main cells and the voltage of the monitor cell ($\Delta V(t) = V_{\text{main}}(t)/m - V_{\text{monitor}}(t)$). $c_{\text{main}}(t) \approx c_{\text{monitor}}(t)$ is satisfied at the beginning of charging or discharging ($t \rightarrow +0$). The $\Delta V(t)$ is given by approximation (C.1) when the current instantly changes.

$$\begin{aligned}\Delta V(+0) &= V_{\text{main}}(+0)/m - V_{\text{monitor}}(+0) \\ &= \{g(c_{\text{main}}(+0)) - r_{\text{rfb}}I\} - g(c_{\text{main}}(t)) \\ &\approx -r_{\text{rfb}}I\end{aligned}\tag{C.1}$$

r_{rfb} is estimated from $\Delta V(+0)$ by using approximation (C.1).

α_c is estimated from the transient behavior of $\Delta V(t)$ explained in Chapter 4. The analysis in Chapter 4 shows that the transient behavior of $\Delta V(t)$ is approximated by equation (C.2).

$$\begin{aligned}\Delta V(t) &\approx g'(c_0)\Delta c(t) - r_{\text{rfb}}I \\ &= -g'(c_0)\frac{I}{WF}\left\{1 - \exp\left(-\frac{t}{\tau_c}\right)\right\} - r_{\text{rfb}}I, \quad \tau_c = \frac{\alpha_c}{W}\end{aligned}\tag{C.2}$$

Here, $c_0 = c_{\text{main}}(0) = c_{\text{monitor}}(0) \approx g^{-1}(V_{\text{monitor}}(0))$. The time constant $\tau_c = \alpha_c/W$ is extracted from the curve of $\Delta V(t)$, and α_c is estimated from the time constant.

α_t is estimated from the steady-state of the charging/discharging behavior. $dc_i(t)/dt$ ($i = \text{main, monitor}$) converges to the value determined by the past load current, as mentioned in Chapter 5. The value is given by $f(I(t - \tau_d))$, as follows.

$$\frac{dc_i(t)}{dt} \rightarrow -\frac{mI(t - \tau_d)}{((m + 1)\alpha_c + \alpha_t)F} = f(I(t - \tau_d)) \quad (\text{C.3})$$

The rate of discharge becomes constant for the fixed current. $c_{\text{monitor}}(t)$ can be estimated from $V_{\text{monitor}}(t)$, and α_t is extracted by differentiating the estimated $c_{\text{monitor}}(t)$.

$$\alpha_t \approx \frac{\Delta t}{\Delta c_{\text{monitor}}(t)} \frac{mI}{F} - (m + 1)\alpha_c \quad (\text{C.4})$$

τ_d is also determined from the estimated value of $c_{\text{monitor}}(t)$. Considering mass balance equation in the monitor cell (4.4), $dc_{\text{monitor}}(t)/dt = 0$ for $t \in [0, \tau_d]$. τ_d is estimated from the term in which $dc_{\text{monitor}}(t)/dt$ is restricted to 0.

Appendix D

Evaluation of approximation

This chapter introduces the approximation of $\Delta V(t)$ at the beginning of charging, and evaluates the error. The EMF of a cell is given by $g(c_i)$ ($i = \text{main, monitor}$). $g(c_i)$ is linearized in the neighborhood of $c_i = c_0$ as following equation (D.1).

$$\begin{aligned} g(c) &= g(c_0) + g'(c_0)(c - c_0) + \mathcal{O}(c - c_0)^2 \\ &\approx g'(c_0)c + g(c_0) + g'(c_0)c_0 \end{aligned} \quad (\text{D.1})$$

c_0 is the initial value of $c_{\text{main}}(t)$ and $c_{\text{monitor}}(t)$. If the linearization has validity, ΔV is represented by approximation (D.2).

$$\begin{aligned} \Delta V(t) &= g(c_{\text{main}}(t)) - r_{\text{fb}}I - g(c_{\text{monitor}}(t)) \\ &\approx \{g'(c_0)c_{\text{main}} + g(c_0) + g'(c_0)c_0\} - r_{\text{fb}}I \\ &\quad - \{g'(c_0)c_{\text{monitor}} + g(c_0) + g'(c_0)c_0\} \\ &= g'(c_0)\Delta c(t) - r_{\text{fb}}I \\ &= -g'(c_0)\frac{I}{WF} \left(1 - e^{-\frac{t}{\tau_c}}\right) - r_{\text{fb}}I, \quad \tau_c = \frac{\alpha_c}{W} \end{aligned} \quad (\text{D.2})$$

Here, $\Delta c(t) = c_{\text{main}}(t) - c_{\text{monitor}}(t)$, and $\Delta c(t)$ is given by equation (4.18).

Approximation (D.2) is compared to the model with transport delay in Chapter 4 in Figure D.1. Figure D.1 shows the error of the approximation compared to the simulation result. The time is rescaled with the time constant $\tau_c = \alpha_c/W$. The error is over 0.01 after $\tau = 0.5$. Thus, τ_c should be extracted from the voltage data within $t = 2\tau_c$ after the beginning of charging.

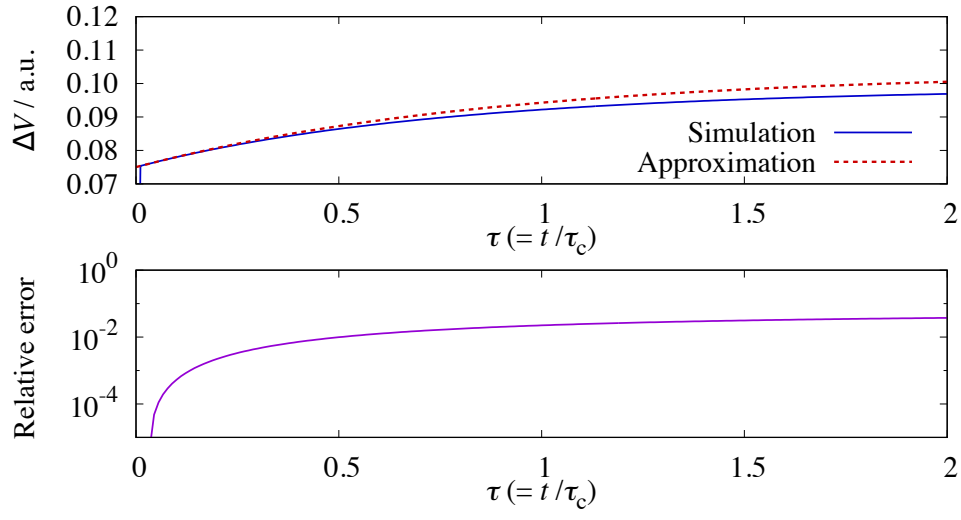


Figure D.1: Approximation error. The error is calculated by the ratio of the absolute error to the simulation. τ is the rescaled time with $\tau_c = 9.0$ s.

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List of Publications

Full length Papers

- 1 Toko Mannari and Takashi Hikiyara, “Transient Behavior of Redox Flow Battery Connected to Circuit Based on Global Phase Structure,” *NOLTA, IEICE*, **9** (1), 137–147 (2018). doi:10.1587/nolta.9.137
- 2 Toko Mannari, Takafumi Okuda, and Takashi Hikiyara, “Model for Charging/Discharging Dynamics of Cells in Redox Flow Battery with Transport Delay,” *Pyisica Scripta*, **94** (9), 095005 (2019). doi:10.1587/nolta.9.137
- 3 Toko Mannari, Takafumi Okuda, and Takashi Hikiyara, “Prediction of Restriction in Output Current by Reactant Flow in Redox Flow Battery for Compensating Load Variations,” *International Journal of Theory and Its Applications* (accepted). doi:10.1002/cta.2881

Proceeding of international conference

Toko Mannari and Takashi Hikiyara, “A Restricting Condition on Transient Behavior of Redox Flow Battery in Phase Space,” *Proc. 2017 IEEE International Telecommunications Energy Conference (IEICE)*, 282–286 (2017). doi:10.1109/INTLEC.2017.8214148

Other international conference

- 1 Toko Mannari, Takafumi Okuda, and Takashi Hikiyara, “Evaluation of the Transient Characteristics of a Redox Flow Battery with Electrolyte Flow,”

The International Flow Battery Forum, Lausanne, Switzerland, 10-12 July, 2018.

- 2 Toko Mannari and Takashi Hikihara, “Effect of Transport Delay on Charging/Discharging Dynamics of Redox Flow Battery under Load Variation,” RISP International Workshop on Nonlinear Circuits, Communications and Signal Processing 2020, Honolulu, Hawaii, 28 February-2 March.

Domestic conference

- 1 Toko Mannari, Minghua Li, and Takashi Hikihara, “A Study on a Current Behavior due to Electrolyte Supply in Redox Flow Battery,” IEICE General Conference 2016, No. A-1-29, Fukuoka, 18 March, 2016.
- 2 Toko Mannari, Minghua Li, and Takashi Hikihara, “A Numerical Study on Discharging Behavior of Redox Flow Battery in Circuit,” 60th Annual Conference of ISCIE, No. 361-1, Kyoto, 27 May, 2016.
- 3 Toko Mannari, Minghua Li, and Takashi Hikihara, “A Numerical Study on Output Behavior of Redox Flow Battery for Load Variation,” IEICE Technical Committee on Nonlinear Problems, No. NLP2016-33, Hokkaido, 21 July, 2016.
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- 5 Toko Mannari and Takashi Hikihara, “A Study on Dynamical Behavior of Redox Flow Battery due to Parameters,” 61st Annual Conference of ISCIE, No. 211-6, Kyoto, 24 May, 2017.
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