



# Mathematical Modeling and Numerical Analysis of Electroless Plating Problem in a Microchannel

Po-Yi Wu

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# Mathematical Modeling and Numerical Analysis of Electroless Plating Problem in a Microchannel

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## COLOPHON

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**Keywords:** electroless plating process, numerical analysis, long time existence

**Mots clés :** dépôt autocatalytique, analyse numérique, existence en temps grand



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# Remerciement





*Je dédie à Linda Chiu*

*À ma famille*

*À Prof. Tony Wen-Hann Sheu*



**Mathematical Modeling and Numerical Analysis of Electroless Plating Problem in a Microchannel****Abstract**

Electroless plating process in microchannel is a rising technology in industry. From a physical point of view, it is a multiphysics problem including fluid dynamics, mass transfer, chemical reaction, phase change, etc.. Especially in micrometer scale, more subtle physical phenomena are of interest. In this thesis, electroless plating problem is mostly taken care by mathematical modeling and numerical analysis. There are three chapters in this thesis: A quick review and introduction of electroless plating process are given in Chapter 1. Analysis of an electroless plating problem in a single phase liquid flow is presented Chapter 2. The numerical simulation on the electroless plating problem with gas generation is discussed in Chapter 3.

- In Chapter 2, the gas generation due to the electroless plating is neglected. Instead, single phase incompressible flow coupled with mass transfer is considered. The small boundary motion owing to the deposited chemical species is modeled by a transpiration approximation. With this simplification, the mathematical model, consists of a Navier-Stokes flow and an equation for the concentration of the plating chemical coupled by non-standard and nonlinear boundary conditions. Existence and uniqueness are proven for the concentration equation. Numerical analysis is carried out and justifies the proposed numerical schemes and nonlinear algorithm.
- In Chapter 3, the gas generation and motion of gaseous phase are taken into account. Since the bubbles are generated randomly and everywhere, a volume averaged two phase flow model is applied. This simplification is coupled with convection-diffusion equations subject to flux boundary conditions satisfying electron balance. A first-order phase volume conservative method and finite element method are carried out for numerical simulation and the well-posedness of numerical scheme is proved. Numerical studies in one and two-dimensional cases with comparison to experiment are performed to justify the proposed model.
- In Appendix B, a further simplified model for chemical species transport in two phase flow is considered. In this case, the convection terms are neglected so that the volume fraction of liquid phase depends only on the concentration of dissolving gas in the electrolyte. Three concentration equations for two chemical species transport and dissolving gas coupling with an ODE for volume fraction of liquid phase are considered. The flux boundary condition on the reacting surface with electron balance is taken care. The existence and uniqueness are proven for the coupling equations. It is shown that the two species case can be generalized to  $N$ -species case.

**Keywords:** electroless plating process, numerical analysis, long time existence

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### Résumé

Le dépôt autocatalytique dans les microcanaux est une technologie en plein essor dans l'industrie. D'un point de vue physique, il s'agit d'un problème multiphysique incluant la dynamique des fluides, le transfert de masse, la réaction chimique, le changement de phase, etc. Surtout à l'échelle micrométrique, des phénomènes physiques plus subtils sont intéressants. Dans cette thèse, le problème du dépôt autocatalytique est principalement traité par la modélisation mathématique et l'analyse numérique. Il y a trois chapitres dans cette thèse : Un examen rapide et une introduction du dépôt autocatalytique sont donnés dans le chapitre 1. L'analyse d'un problème de dépôt autocatalytique dans un écoulement de liquide monophasique est présentée au chapitre 2. La simulation numérique du problème de dépôt électrolytique avec la production de gaz est abordée au chapitre 3.

- Dans le chapitre 2, la génération de gaz due au dépôt autocatalytique est négligée. Au lieu de cela, un écoulement incompressible monophasé couplé à un transfert de masse est considéré. Le petit mouvement de frontière dû aux espèces chimiques déposées est modélisé par une approximation de la transpiration. Avec cette simplification, le modèle mathématique se compose d'un écoulement Navier-Stokes et d'une équation pour la concentration du produit chimique de dépôt couplée par des conditions aux limites non standard et non linéaires. L'existence et l'unicité sont prouvées pour l'équation de concentration. Une analyse numérique est réalisée qui justifie les schémas numériques et l'algorithme non linéaire proposés.
- Dans le chapitre 3, la génération de gaz et le mouvement de la phase gazeuse sont pris en compte. Étant donné que les bulles sont générées de manière aléatoire et partout, un modèle d'écoulement à deux phases moyennées en volume est appliqué. Cette simplification est couplée à des équations de convection-diffusion soumises à des conditions aux limites de flux satisfaisant l'équilibre électrostatique. Une méthode conservatrice de volume de phase du premier ordre et une méthode d'éléments finis sont effectuées pour la simulation numérique et le bien-fondé du schéma numérique est prouvé. Des études numériques dans des cas uni et bidimensionnels avec comparaison à l'expérience sont réalisées pour justifier le modèle proposé.
- Dans l'annexe B, un autre modèle simplifié pour le transport d'espèces chimiques dans un écoulement à deux phases est considéré. Dans ce cas, les termes de convection sont négligés de sorte que la fraction volumique de phase liquide ne dépend que de la concentration en gaz de dissolution dans l'électrolyte. On considère trois équations de concentration pour le transport de deux espèces chimiques et le couplage du gaz de dissolution avec une ODE pour la fraction volumique de la phase liquide. La condition aux limites de flux sur la surface de réaction avec équilibre électrostatique est prise en compte. L'existence et l'unicité sont prouvées pour les équations de couplage. On montre que le cas des deux espèces peut être généralisé au cas des  $N$ -espèces.

**Mots clés :** dépôt autocatalytique, analyse numérique, existence en temps grand

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# Chapter 1

## Introduction and state of the art

### 1.1 Electroless plating process

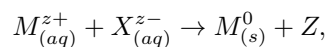
#### 1.1.1 Overview

Electroless plating is a class of industrial chemical reaction process aimed at forming a film or layer on a base substrate by reducing complex metal cations in a liquid solution [15, 94, 80]. In contrast to electroplating processes, the reduction of metal cations can be achieved without the external current during electroless plating process. The metal coatings is created by autocatalytic chemical reduction of metal cations in a liquid bath. This technique has been widely applied in various industries. For instance, surface decoration, hard-wearing coating, manufacture of hard-disc drive, printed circuit boards, etc.[80, 106].

Recently, electroless process in microfluidic channels has been regarded as a promising micro or nano meter technology. Applications range from chemical etching process for electronic devices, to electrical packaging for food [93, 79]. Compared to the large-scale electroless process, the change of geometry to the micro- or nano-meter scale raises a critical issue for the deposition as the thickness becomes comparable to the dimension of flow channel. For instance, in the copper interconnecting process [67] by electroless plating, the thickness of the deposition layer of copper is large enough to risk a connection of the pillars.

#### 1.1.2 Mechanism

In general, the chemical reaction of electroless plating can be expressed as



where  $M$  is the metal,  $X^{z-}$  is the reducing agent, and  $Z$  is its oxidized by product.

In order to deposit the metal uniformly on a reaction surface, an initiator that is either an additional catalyst or the substrate itself shall be added in advance. Moreover, the reaction must be autocatalytic so that it continues after the reaction surface has been covered by the metal. For the setting of the electroless plating process, see also Figure 1.1.

#### 1.1.3 Mixed potential theory

Two assumption is made when the mixed potential theory is applied for the electroless plating process: (i) The overall chemical reaction can be divided into several partial reactions. Each

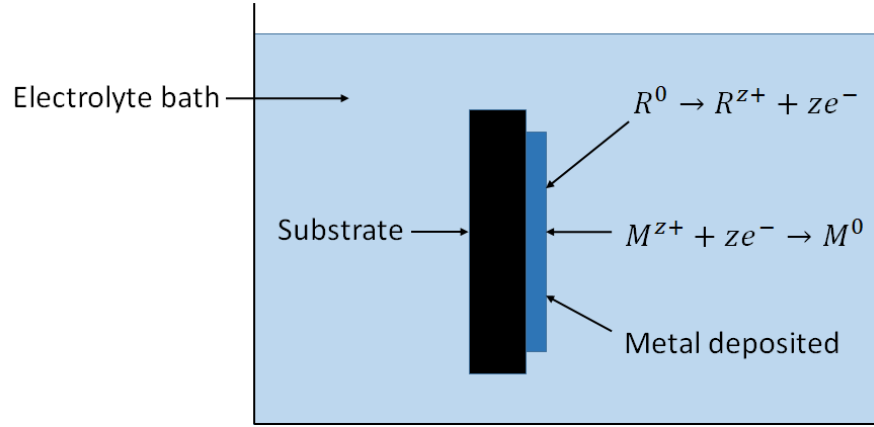


Figure 1.1: Schematic of electroless plating setup.

partial reaction belongs to either anodic part or cathodic part. Here, the anodic reaction is the decomposition of the reducing agent



and the cathodic reaction the reduction of the metal complex cations



(ii) The reaction must satisfy electron balance at all time. Therefore, the sum of the anodic current density and the cathodic current density is zero. That is,

$$\sum_{j \in \text{anodic}} I_j + \sum_{j \in \text{cathodic}} I_j = 0. \quad (1.3)$$

We denote the equilibrium potential for species  $j$  by  $E_j$ , the Butler-Volmer equation (see for example [8]) suggest that the current density  $I_j$  can be expressed as

$$I_j = i_j c_j^{\gamma_j} := A_j \left[ \exp \left( \frac{\alpha_j z_j F \xi_j}{R\theta} \right) - \exp \left( \frac{-\beta_j z_j F \xi_j}{R\theta} \right) \right] c_j^{\gamma_j}, \quad (1.4)$$

where  $A_j$  is the ratio of the reference current density and the corresponding reference species concentration,  $\alpha_j$  the anodic transfer coefficient,  $\beta_j$  the cathodic transfer coefficient,  $z_j$  the number of electrons,  $F$  the Faraday constant,  $R$  the gas constant,  $\theta$  the temperature,  $c_j$  the species concentration, and  $\gamma_j$  the concentration dependency. In the above,  $\xi_j$  is the overpotential which can be expressed as

$$\xi_j = E_{mix} - E_j, \quad (1.5)$$

where  $E_{mix}$  is the mixed potential (see also Figure 1.2).

#### 1.1.4 Electroless plating in a microchannel

As the size of channel becomes smaller, more subtle issues influencing the deposition quality shall be taken into account. Those effects that do not play crucial roles in a large size problem become

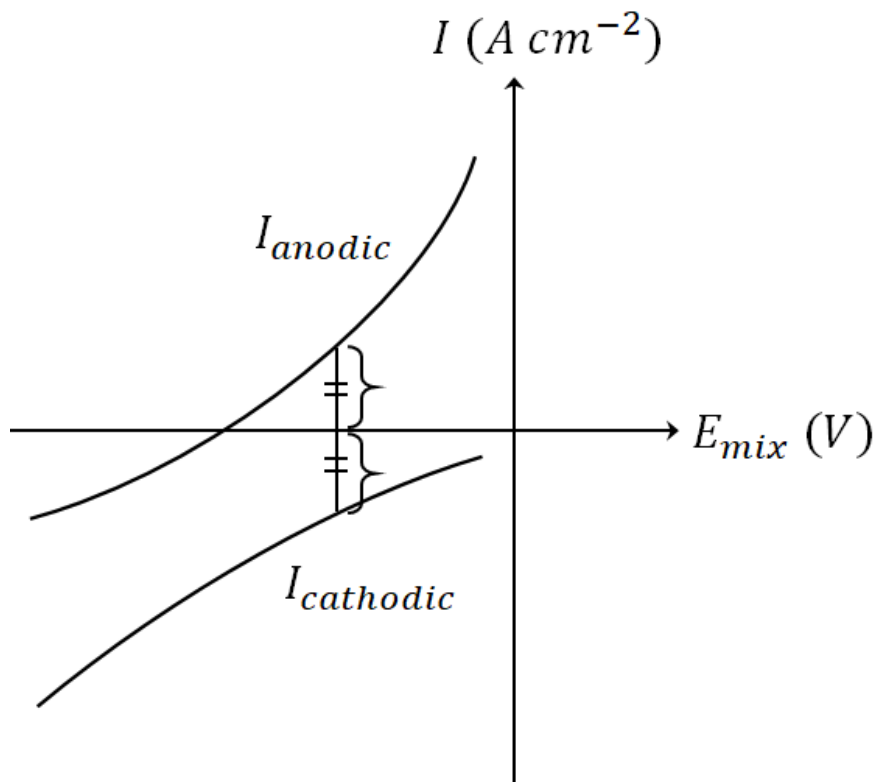


Figure 1.2: Current-potential curves for the system satisfying the hypotheses of the mixed potential theory.

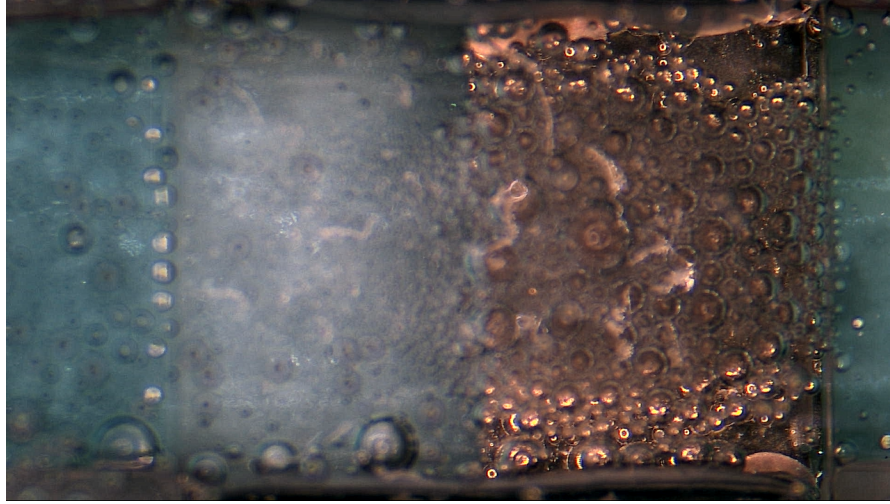


Figure 1.3: A microchannel of cross section  $8\text{ mm} \times 1\text{ mm}$  with a copper plate where the electroless copper plating process occurs.

main characters in micro- or nano-scale. Some issues which are worthy of further consideration for electroless plating in a microchannel are listed below.

### Gas generation

In a large scale problem, the gas generation in the electroless plating process is not important because it takes only slight space in comparison with the size of bath. In contrast, the effect that bubbles prevent the substrate from being plated is serious when the flow channel is of smaller size. Indeed, conducting an electroless copper plating in a microchannel with cross section of size  $8\text{ mm} \times 1\text{ mm}$  for 2 minutes, the bubbles will have been taken over a large portion of the channel (see Figure 1.3).

Whether the gas generation occurs is determined by the electroless plating system being employed. Electroless nickel and copper plating systems generate hydrogen gas. On the other hand, electroless gold does not generate gas. Given this fact, both single phase and two-phase flow problems for the fluid motion in an electroless plating process play crucial roles.

### Seams and voids between microbumps

Microbump bonding is one of the important applications of electroless plating in microchannels. The geometry effect arising from the shape of microbumps is significant for the plating quality. For example, if two microbumps to be plated are flat-topped (see Figure 1.4a), then seams or voids may appear in the jointed bumps [67, 127]. This is owing to the fact that the region between two bumps is always of the lowest ionic concentration. The deposition rate of the outer region is always higher than the inner region between two bumps. Once the inner region is closed by the deposited metal of outer region, the seam or void remains due to the shortage of fresh electrolyte. On the other hand, if the dome-shaped microbumps (see Figure 1.4b) are adopted for electroless plating process, the bumps can be jointed perfectly.

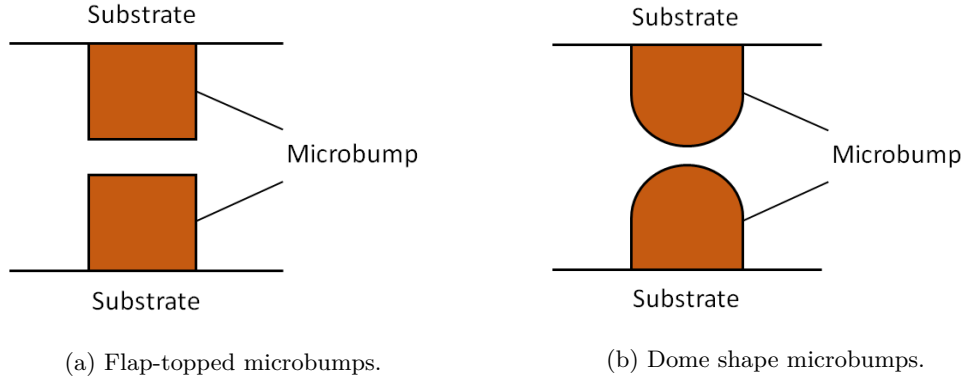


Figure 1.4: Comparison between flat-topped bump and dome shape microbumps.

### Bridging

For a circuit pattern, It is essential to control precisely where to be plated and not to be plated. Let us take the bonding of face-to-face microbump array as an illustration. In most cases, the desired region to be plated is the gap between face-to-face bumps. Conversely, the plane within the bumps installed on the same substrate are not desired to be deposited since the short circuit will be caused by the connection between to bumps on the same plane. Such undesired phenomenon is called *bridging* [24, 126]. Bridging is due to the instability of the electrolyte which causes a homogeneous decomposition so that the metal particles accumulate everywhere. Indeed, this phenomenon is observed in the low flow velocity region where the ionic concentration is sufficient but the metal particles cannot be moved away.

### Uniformity

For many circuit board, there always exists period structure so that the uniformity of plating quality is important. However, many physical conditions in such periodic space may not be uniform. For example, the bubble distribution is in general far from uniform even in a microchannel with simple geometry (see Figure. 1.3)

To see another uniformity issue, we take the bonding of face-to-face microbump arrays as an example again. Considering an face-to-face array of microbumps is placed in a microchannel, we observed that the plating condition is highly nonuniform [126]. The most interesting observation is that the bumps near the flow entrance, which were in the region of higher ionic concentration, were not deposited. A hypothesis is that the metal particles near the entrance was washed away by the fluid flow but deposit behind. Indeed, when the entrance velocity is sufficiently high, None of the microbumps can be plated.

## 1.2 Mathematical model for electroless plating problem

Electroless plating problem can be regarded as a multiphysics problem which consists of surface reaction, fluid dynamics, heat transfer, chemical potential distribution, etc.. In a large scale deposition, simplified models would be adequate for describing the occurring physical phenomena, especially in a simple geometry case. In what follows, we review two kinds of one-dimensional models which well described the electroless plating process in the special cases.

### 1.2.1 One-dimensional steady state advection-diffusion equations

Kim and Sohn proposed a model describing the concentration profile of chemical species in the diffusion layer of a plated rotating disk with constant angular velocity [66]. In this situation, the fluid flow near the surface of rotating disk can be approximated by a uniformly distributed flow directing to the surface. In addition, the thickness of diffusion layer is approximately uniform on the surface. Consequently, the physical domain for modeling can be reduced to be one-dimensional (see Chapter II, Section 11 in [74] for the derivation).

The modeling problem is given as follows: Let  $c_j$  be the concentration profile of the  $j$ -th species. The governing equations for steady state problem is

$$-D_j \frac{\partial^2 c_j}{\partial z^2} + v \frac{\partial c_j}{\partial z} = 0, \quad (1.6)$$

where  $D_j$  is the diffusion coefficient,  $v$  the velocity field given by

$$v = -az^2\omega^{3/2}\nu^{-1/2}, \quad (1.7)$$

where  $a = 0.51023$ ,  $\omega$  is the angular velocity of the rotating disk, and  $\nu$  the kinematic viscosity of the electrolyte. The boundary conditions are given by

$$c_j = c_{b,j}, \quad z^2 + r^2 \rightarrow \infty, \quad -D_j \frac{\partial c_j}{\partial z} = \sum_{j \in R_j} \frac{|I_j|}{z_j F}, \quad z = 0, \quad (1.8)$$

where  $c_{b,j}$  is the bulk concentration of species  $j$ ,  $R_j$  the set collecting those species  $j$  participating in the reaction related to  $c_j$ ,  $z_j$  the number of electrons,  $F$  the Faraday constant, and  $I_j$  the current density. We recall that  $I_j$  can be expressed by (1.4) with the overpotential (1.5).

For numerical simulation, the Dirichlet boundary condition  $c_j = c_{b,j}$  shall be set at the diffusion layer-bulk interface. The diffusion layer thickness  $\delta_j$  at steady state for a rotating disk can be expressed as

$$\delta_j = 1.61 D_j^{1/3} \omega^{-1/2} \nu^{1/6}. \quad (1.9)$$

Finally, the system of equations can be closed by the electron balance condition (1.3).

### 1.2.2 One-dimensional time-dependent diffusion-migration equations

To simulate electroless copper plating on a planar substrate, Ramasubramanian et. al. [100] applied a system of time-dependent diffusion-migration equations for solving the concentration profile of each species participating in the electroless process.

Let  $c_j$ ,  $j = 1, \dots, N$  be the concentration profile of the  $j$ -th species. In the diffusion layer, the mass balance implies that

$$\frac{\partial c_j}{\partial t} = -\frac{\partial J_j}{\partial z} + Y_j, \quad (1.10)$$

where  $Y_j$  is the rate of homogeneous production or consumption of species  $j$  and the flux  $J_j$  is contributed by diffusion and migration:

$$J_j = -\frac{z_j D_j F c_j}{R\theta} \frac{\partial \Phi}{\partial z} - D_j \frac{\partial c_j}{\partial z}. \quad (1.11)$$

In the above  $\Phi$  is the solution potential. In the electrolyte, water equilibrium holds at all times

and therefore we have

$$\sum_j z_j c_j = 0, \quad (1.12)$$

which closes the system with unknowns  $(c_1, \dots, c_N, \Phi)$ .

The boundary conditions are similar to those proposed by Kim and Sohn [66]. At the diffusion layer-bulk interface, we let

$$c_j = c_{b,j}$$

At the electrode surface, the Neumann boundary conditions are given similarly the second equation of (1.8) but the current densities take the form

$$\begin{aligned} I_a &= A_a \left\{ \prod_{k \in R_a} c_k^{\gamma_k} \left( \exp \left( \frac{\alpha_a F}{R\theta} [V - \Phi - U_j^0] \right) - \exp \left( \frac{-\beta_a F}{R\theta} [V - \Phi - U_j^0] \right) \right) \right\}, \\ I_c &= A_c \left\{ \prod_{k \in R_c} c_k^{\gamma_k} \left( \exp \left( \frac{\alpha_c F}{R\theta} [V - \Phi - U_j^0] \right) - \exp \left( \frac{-\beta_c F}{R\theta} [V - \Phi - U_j^0] \right) \right) \right\}, \end{aligned} \quad (1.13)$$

where  $R_a$  and  $R_c$  are the set of species  $j$  involving in anodic reaction and cathodic reaction, respectively,  $V$  is the electrode potential, and  $U_j^0$  is the open-circuit potential for the  $j$ -th species. Here,  $V$  plays a similar role as the mixed potential  $E_{mix}$  in (1.5). The full system can be closed by the electron balance on the reacting surface:

$$I_a + I_c = 0. \quad (1.14)$$

## 1.3 Governing equations of interest in an electroless plating problem

### 1.3.1 Navier-Stokes equations

To derive the Navier-Stokes equations, we assume that the fluid is a continuum and all the fields of interest, such as density, flow velocity, pressure, and temperature are differentiable.

#### Material derivative

Changes of a physical quantity can be measured in two different ways depending on where the observer is: One can measure a physical quantity either (i) on a fixed point (Eulerian), or (ii) by following a parcel of fluid along its streamline (Lagrangian). The derivative of a physical quantity with respect to a fixed position in space is called a Eulerian derivative, while the derivative following the flow velocity is called a Lagrangian derivative. Based on the relation between Eulerian and Lagrangian derivative, we define the material derivative which connects these two concept:

$$\frac{D}{Dt} := \partial_t + \mathbf{u} \cdot \nabla, \quad (1.15)$$

where  $\mathbf{u}$  is the flow velocity.



### Continuity equation

Let  $\phi$  be any physical quantity defined over a control volume  $\Omega$ , and  $\Gamma$  its boundary. The mass conservation can be expressed as

$$\frac{d}{dt} \int_{\Omega} \phi dx = \int_{\Gamma} \phi \mathbf{u} \cdot \mathbf{n} dS - \int_{\Omega} s dx, \quad (1.16)$$

where  $\mathbf{u}$  is the flow velocity of the field,  $\mathbf{n}$  is the outward unit normal, and  $s$  is the sink or source in the flow. By the divergence theorem, we have

$$\frac{d}{dt} \int_{\Omega} \phi dx = - \int_{\Omega} \nabla \cdot (\phi \mathbf{u}) dx - \int_{\Omega} s dx. \quad (1.17)$$

Applying the Reynolds transport theorem, we have

$$\int_{\Omega} \partial_t \phi dx = - \int_{\Omega} \nabla \cdot (\phi \mathbf{u}) dx - \int_{\Omega} s dx. \quad (1.18)$$

The above equation must hold for any control volume. Therefore,

$$\partial_t \phi + \nabla \cdot (\phi \mathbf{u}) + s = 0 \quad (1.19)$$

### Conservation of mass

Replacing  $\phi$  by the density  $\rho$  in (1.19), and assuming that there is no source or sink of mass, we have

$$\partial_t \rho + \nabla \cdot (\rho \mathbf{u}) = 0. \quad (1.20)$$

### Conservation of momentum

Let  $\phi = \rho \mathbf{u}$  in (1.19), we have

$$\partial_t (\rho \mathbf{u}) + \nabla \cdot (\rho \mathbf{u} \otimes \mathbf{u}) = \mathbf{s}, \quad (1.21)$$

where  $\mathbf{s}$  is a vector function. The above equation can be split as

$$(\partial_t \rho) \mathbf{u} + \rho \partial_t \mathbf{u} + (\mathbf{u} \cdot \nabla \rho) \mathbf{u} + \rho (\mathbf{u} \cdot \nabla) \mathbf{u} + \rho (\nabla \cdot \mathbf{u}) \mathbf{u} = \mathbf{s}. \quad (1.22)$$

The rearrangement gives

$$\begin{aligned} & (\partial_t \rho + \mathbf{u} \cdot \nabla \rho + \rho \nabla \cdot \mathbf{u}) \mathbf{u} + \rho (\partial_t \mathbf{u} + (\mathbf{u} \cdot \nabla) \mathbf{u}) \\ &= (\partial_t \rho + \nabla \cdot (\rho \mathbf{u})) \mathbf{u} + \rho (\partial_t \mathbf{u} + (\mathbf{u} \cdot \nabla) \mathbf{u}) = \mathbf{s} \end{aligned} \quad (1.23)$$

By (1.15) and (1.20), we get

$$\rho \frac{D\mathbf{u}}{Dt} = \rho (\partial_t \mathbf{u} + (\mathbf{u} \cdot \nabla) \mathbf{u}) = \mathbf{s} \quad (1.24)$$

### Cauchy momentum equation

The momentum source  $\mathbf{s}$  can be split into two terms: one term for internal stresses and another for external forces. The momentum equation can be expressed as

$$\rho \frac{D\mathbf{u}}{Dt} = \nabla \cdot \boldsymbol{\sigma} + \mathbf{f}, \quad (1.25)$$

where  $\boldsymbol{\sigma}$  is the Cauchy stress tensor and  $\mathbf{f}$  is the body force.

In three dimensional space,  $\boldsymbol{\sigma}$  is a rank two symmetric tensor which can be explicitly represented as a  $3 \times 3$  matrix

$$\boldsymbol{\sigma} = \begin{pmatrix} \sigma_{xx} & \tau_{xy} & \tau_{xz} \\ \tau_{yx} & \sigma_{yy} & \tau_{yz} \\ \tau_{zx} & \tau_{zy} & \sigma_{zz} \end{pmatrix} \quad (1.26)$$

In the above,  $\boldsymbol{\sigma}$  can be further split into isotropic part standing for the normal stresses and anisotropic part for shear stresses:

$$\begin{aligned} \boldsymbol{\sigma} &= \begin{pmatrix} \sigma_{xx} & \tau_{xy} & \tau_{xz} \\ \tau_{yx} & \sigma_{yy} & \tau_{yz} \\ \tau_{zx} & \tau_{zy} & \sigma_{zz} \end{pmatrix} = - \begin{pmatrix} p & 0 & 0 \\ 0 & p & 0 \\ 0 & 0 & p \end{pmatrix} + \begin{pmatrix} \sigma_{xx} + p & \tau_{xy} & \tau_{xz} \\ \tau_{yx} & \sigma_{yy} + p & \tau_{yz} \\ \tau_{zx} & \tau_{zy} & \sigma_{zz} + p \end{pmatrix} \\ &= -p\mathbf{I} + \boldsymbol{\tau}, \end{aligned} \quad (1.27)$$

where  $\mathbf{I}$  is the identity matrix, and  $\boldsymbol{\tau}$  is the deviatoric stress tensor. Since the tensor  $\boldsymbol{\tau}$  should be zero when the fluid is motionless, we define the mechanical pressure  $p$  by

$$p = -\frac{1}{3}(\sigma_{xx} + \sigma_{yy} + \sigma_{zz}). \quad (1.28)$$

Finally, the Cauchy equation can be expressed as

$$\rho \frac{D\mathbf{u}}{Dt} = -\nabla p + \nabla \cdot \boldsymbol{\tau} + \mathbf{f}. \quad (1.29)$$

### 1.3.2 Compressible and incompressible flow

#### Compressible flow

We assume that the Cauchy stress tensor  $\boldsymbol{\tau}$  in (1.29) satisfying the following assumptions

1.  $\boldsymbol{\tau}$  is Galilean invariant: it depends only on the spatial derivatives of the flow velocity. That is,  $\boldsymbol{\tau}$  is a function of  $\nabla \mathbf{u}$ .
2. The stress  $\boldsymbol{\tau}$  is linear in the variable  $\boldsymbol{\tau}(\nabla \mathbf{u}) = \mathbf{C} : \nabla \mathbf{u}$  for some fourth-order constant tensor.
3. The fluid is isotropic. By Helmholtz decomposition  $\boldsymbol{\tau}$  can be expressed in terms of two scalar Lamé parameters: the bulk viscosity  $\lambda$  and the dynamic viscosity  $\mu$ , i.e.

$$\boldsymbol{\tau} = \lambda(\nabla \cdot \mathbf{u})\mathbf{I} + 2\mu\boldsymbol{\varepsilon}, \quad (1.30)$$

where  $\mathbf{I}$  is the identity tensor and  $\boldsymbol{\varepsilon}(\nabla \mathbf{u}) = \frac{1}{2}\nabla \mathbf{u} + \frac{1}{2}(\nabla \mathbf{u})^T$ .

In three-dimension, given that  $\text{tr}(\varepsilon) = \nabla \cdot \mathbf{u}$  and  $\text{tr}(\boldsymbol{\tau}) = (3\lambda + 2\mu)\nabla \mathbf{u}$ ,  $\boldsymbol{\tau}$  can be split into isotropic and deviatoric parts:

$$\boldsymbol{\tau} = (\lambda + \frac{2}{3}\mu)(\nabla \cdot \mathbf{u})I + \mu(\nabla \mathbf{u} + (\nabla \mathbf{u})^T - \frac{2}{3}(\nabla \cdot \mathbf{u})I). \quad (1.31)$$

Introducing the second viscosity  $\zeta := \lambda + \frac{2}{3}\mu$ , the linear stress constitutive equation can be expressed as

$$\boldsymbol{\tau} = \zeta(\nabla \cdot \mathbf{u})I + \mu(\nabla \mathbf{u} + (\nabla \mathbf{u})^T - \frac{2}{3}(\nabla \cdot \mathbf{u})I). \quad (1.32)$$

Let  $\bar{p} := p - \zeta \nabla \mathbf{u}$ , we obtain the Navier-Stokes momentum equation

$$\rho(\partial_t \mathbf{u} + (\mathbf{u} \cdot \nabla) \mathbf{u}) = -\nabla \bar{p} + \nabla \cdot \left( \mu(\nabla \mathbf{u} + (\nabla \mathbf{u})^T - \frac{2}{3}(\nabla \cdot \mathbf{u})I) \right) + \mathbf{f}. \quad (1.33)$$

Applying the relation  $\nabla \cdot (\nabla \mathbf{u})^T = \nabla(\nabla \cdot \mathbf{u})$ , we finally get

$$\rho(\partial_t \mathbf{u} + (\mathbf{u} \cdot \nabla) \mathbf{u}) = -\nabla \bar{p} + \mu \Delta \mathbf{u} + \frac{1}{3}\mu \nabla(\nabla \cdot \mathbf{u}) + \mathbf{f}. \quad (1.34)$$

**Remark 1.3.1** In two dimension, we have

$$\rho(\partial_t \mathbf{u} + (\mathbf{u} \cdot \nabla) \mathbf{u}) = -\nabla \bar{p} + \mu \Delta \mathbf{u} + \mathbf{f}. \quad (1.35)$$

### Incompressible flow

The incompressibility implies that the material derivative of the density is zero, i.e.,

$$\frac{D\rho}{Dt} = 0. \quad (1.36)$$

Combining the above equation with the continuity equation (1.20), we have

$$\nabla \cdot \mathbf{u} = 0. \quad (1.37)$$

Therefore, the linear stress constitutive equation for the incompressible flow can be written as

$$\boldsymbol{\tau} = \mu(\nabla \mathbf{u} + (\nabla \mathbf{u})^T). \quad (1.38)$$

If  $\mu$  is constant, divergence of the deviatoric stress is given by

$$\nabla \cdot \boldsymbol{\tau} = \nabla \cdot (\nabla \mathbf{u} + (\nabla \mathbf{u})^T) = \mu \Delta \mathbf{u}. \quad (1.39)$$

Furthermore, if  $\rho$  is constant, the incompressible Navier-Stokes equation can be expressed as

$$\partial_t \mathbf{u} + (\mathbf{u} \cdot \nabla) \mathbf{u} - \nu \Delta \mathbf{u} = -\nabla \tilde{p} + \tilde{\mathbf{f}}, \quad (1.40)$$

where  $\nu = \mu/\rho$ ,  $\tilde{p} = \bar{p}/\rho$ ,  $\tilde{\mathbf{f}} = \frac{1}{\rho}\mathbf{f}$ .

### 1.3.3 Gas-liquid two phase flow

In electroless copper and nickel plating system, hydrogen gas generation is a crucial issue, especially in a microchannel, since the volume of gas is comparable to the size of the physical domain. Therefore, the governing equations for gas-liquid two phase flow should be considered.

There are several versions of models describing the two phase flow. They can be roughly divided into two classes: (i) The interfaces of heterogeneous phases can be explicitly captured; (ii) The distribution of phases is somehow stochastic so that the problem can only be described in an average sense. For electroless plating process with gaseous phase generation, the problem at the beginning before a serious aggregation of bubbles is of class (ii). Once some large bubbles has accumulated in the microchannel, the problem becomes class (i) in a sense of approximation. Now we are in a position to introduce some governing equations in the aspect of these two classes.

#### Diffuse interface models

To formulate the thermodynamics and transport phenomena of multiphase systems, Reyleigh [77] and van der Waals [119] proposed a so-called diffuse interface model which assumes that the heterogeneous interfaces have a non-zero thickness. Based on this idea, several Navier-Stokes/Cahn-Hilliard system were proposed for modeling the multiphase flow [1, 60, 78]. For example, the *model H* for incompressible two phase flow proposed by Hohenberg and Halperin [60] can be read as

$$\begin{aligned} \rho \partial_t \mathbf{u} + \rho (\mathbf{u} \cdot \nabla) \mathbf{u} - \nabla \cdot (\eta(c)(\nabla \mathbf{u} + (\nabla \mathbf{u})^T)) + \nabla p &= \hat{\sigma} \epsilon \nabla \cdot (\nabla c \otimes c), \\ \nabla \cdot \mathbf{u} &= 0, \\ \partial_t c + \mathbf{u} \cdot \nabla c &= \nabla \cdot (m \nabla \mu), \\ \mu &= \hat{\sigma} \epsilon^{-1} \Psi'(c) - \hat{\sigma} \epsilon \Delta c. \end{aligned} \tag{1.41}$$

In the above,  $\rho$  is the density,  $\mathbf{u}$  is the mean velocity of fluids,  $p$  is the pressure and  $c$  is an order parameter corresponding to the concentration of the fluids (e.g. concentration of one component or concentration difference between two components),  $\eta(c)$  is the viscosity of the mixture,  $\hat{\sigma}$  is the surface energy density  $\epsilon$  is a parameter related to the thickness of the interface,  $\Psi$  is a homogeneous free energy density and  $\mu$  is the chemical potential.

Another example proposed by Abels [1] is a thermodynamically consistent generalization of (1.41) to the case of non-matched densities based on a divergence-free velocity field  $\mathbf{u}$ . The governing equations can be expressed as

$$\begin{aligned} \partial_t(\rho \mathbf{u}) + \nabla \cdot (\rho \mathbf{u} \otimes \mathbf{u}) + \nabla \cdot (\mathbf{u} \otimes \frac{\tilde{\rho}_1 - \tilde{\rho}_2}{2} m(\varphi) \nabla \mu) \\ - \nabla \cdot (\eta(\varphi)(\nabla \mathbf{u} + (\nabla \mathbf{u})^T)) + \nabla p &= -\hat{\sigma} \epsilon \nabla \cdot (\nabla \varphi \otimes \nabla \varphi), \\ \nabla \cdot \mathbf{u} &= 0, \\ \partial_t \varphi + \mathbf{u} \cdot \nabla \varphi &= \nabla \cdot (m(\varphi) \nabla \mu) \\ \mu &= \hat{\sigma} \epsilon^{-1} \Psi'(\varphi) - \hat{\sigma} \epsilon \Delta \varphi, \end{aligned} \tag{1.42}$$

where  $\varphi = \varphi_2 - \varphi_1$  is the difference of the volume fractions and  $\tilde{\rho}_2 - \tilde{\rho}_1$  is the difference of the densities. The above model has been widely used for numerical simulation (e.g. [107, 58, 114]).

### Level set model

Unlike the diffuse interface model, the interface between two phases formulated by the level set model is sharp, i.e., the thickness of the interface between two phases is zero. In this case, the equation of motion for incompressible two phase flow is described by [112]

$$\begin{aligned}\partial_t \mathbf{u} + (\mathbf{u} \cdot \nabla) \mathbf{u} &= \frac{1}{\rho} (\nabla \cdot (\mu(\nabla \mathbf{u} + (\nabla \mathbf{u})^T))) - \nabla p + \sigma \kappa \delta(d) \mathbf{n} + \tilde{\mathbf{f}}, \\ \nabla \cdot \mathbf{u} &= 0,\end{aligned}\tag{1.43}$$

where  $\mathbf{u} = \mathbf{u}(x, t)$  is the fluid velocity,  $\rho = \rho(x, t)$  is the fluid density,  $\mu = \mu(x, t)$  is the fluid viscosity, and  $\tilde{\mathbf{f}}$  is the body force. The surface tension is assumed to be a force exerting only on the interface. We denote by  $\sigma$  the surface tension,  $\kappa$  the curvature of the interface,  $d$  the normal distance to the interface,  $\delta$  the Dirac delta function, and  $\mathbf{n}$  the unit outward normal at the interface.

For immiscible fluids, the density and viscosity are constant along the path of velocity field. Therefore, we have

$$\begin{aligned}\partial_t \rho + (\mathbf{u} \cdot \nabla) \rho &= 0 \\ \partial_t \mu + (\mathbf{u} \cdot \nabla) \mu &= 0.\end{aligned}\tag{1.44}$$

Let  $\rho_1, \mu_1$  denote the density and viscosity of the gaseous phase fluid, respectively, and for liquid phase,  $\rho_2, \mu_2$ . The level set  $\phi$  is defined to discriminate the phases. For example,  $\phi$  satisfies the following properties

$$\rho = \begin{cases} \rho_2, & \text{if } \phi > 0 \\ \rho_1, & \text{if } \phi < 0 \\ \frac{\rho_1 + \rho_2}{2}, & \text{if } \phi = 0 \end{cases}\tag{1.45}$$

and

$$\mu = \begin{cases} \mu_2, & \text{if } \phi > 0 \\ \mu_1, & \text{if } \phi < 0 \\ \frac{\mu_1 + \mu_2}{2}, & \text{if } \phi = 0. \end{cases}\tag{1.46}$$

Moreover,  $\phi$  is carried by the velocity field

$$\partial_t \phi + (\mathbf{u} \cdot \nabla) \phi = 0.\tag{1.47}$$

If we initialize  $\phi$  to be the signed distance function from the interface,  $\phi$  is smooth, unlike  $\rho$  and  $\mu$ . This shows the advantage to solve  $\phi$  numerically.

To avoid the instability caused by the sharp changing of density and viscosity at the interface, a smoothing procedure on these two quantities is often applied to modify the governing equation, which leads to a similar idea as the diffuse interface model. Here is a common example of smoothing on the density: the density  $\rho$  can be smoothed by acting with a smoothed Heaviside function  $H_\alpha$  defined by

$$H_\alpha(\phi) := \begin{cases} 1, & \text{if } \phi > \alpha, \\ 0, & \text{if } \phi < -\alpha, \\ \frac{1}{2} \left( 1 + \frac{\phi}{\alpha} + \frac{1}{\pi} \sin\left(\frac{\pi\phi}{\alpha}\right) \right), & \text{otherwise.} \end{cases}\tag{1.48}$$

Now the smoothed density can be defined by

$$\rho(\phi) = \rho_2 H_\alpha(\phi) + \rho_1(1 - H_\alpha(\phi)). \quad (1.49)$$

It is worth noting that the smoothing in the diffuse interface model is by hypothesis but it is artificially made in the level set model.

### Averaged two phase flow model

When the distribution of dispersive phases in a physical domain is stochastic, we may describe it in terms of the volume fraction of each phase at each point of the physical domain. The volume fraction of a phase can be regarded as the expectation that the phase occurs at a given point. This macroscopic aspect to the phase distribution is called volume averaging.

We review the derivation of volume averaging formulae introduced in [85, 41]. Let  $V_0$  be an elementary volume to be observed in and  $V_k$  the volume in  $V_0$  occupied by a single phase  $k$  and bounded by the interface  $A_k$ , which is assumed to be oriented. Let  $\mathbf{n}_k$  be a outer normal to  $A_k$  and  $\mathbf{w}_k$  the normal velocity of  $A_k$ .

The volume average of some quantity  $\Psi$  in phase  $k$  is

$$\langle \Psi \rangle_k = \frac{1}{V_0} \int_{V_0} \chi_k \Psi dx, \quad (1.50)$$

where  $\chi_k$  is the indicator function that is 1 of  $V_k$ . The intrinsic volume average is defined by

$$\langle \Psi \rangle_k^{(k)} = \frac{1}{V_k} \langle \Psi \rangle_k \text{ where } V_k = \int_{V_0} \chi_k dx \quad (1.51)$$

We define the volume fraction  $r_k = \frac{V_k}{V_0}$  with the properties  $\sum_k r_k = 1$  and

$$\langle \Psi \rangle_k = r_k \langle \Psi \rangle_k^{(k)}. \quad (1.52)$$

Some useful formulae in terms of the averaging are listed below[123, 109]:

$$\left\langle \frac{\partial \Psi}{\partial t} \right\rangle_k = \frac{\partial \langle \Psi \rangle_k}{\partial t} - \frac{1}{V_0} \int_{A_k} \Psi_k \mathbf{w}_k \cdot \mathbf{n}_k dA, \quad (1.53)$$

$$\langle \nabla \Psi \rangle_k = \nabla \langle \Psi \rangle_k + \frac{1}{V_0} \int_{A_k} \Psi_k \mathbf{n}_k dA. \quad (1.54)$$

If  $\Psi$  is a vector, we also have

$$\langle \nabla \cdot \Psi \rangle_k = \nabla \cdot \langle \Psi \rangle_k + \frac{1}{V_0} \int_{A_k} \Psi \cdot \mathbf{n}_k dA. \quad (1.55)$$

**Remark 1.3.2** If  $\Psi = 0$  outside  $V_k$  then we have

$$-\frac{1}{V_0} \int_{A_k} \Psi \cdot \mathbf{n}_k dA = -\frac{1}{V_0} \int_{V_k} \nabla \cdot \Psi dV = -\frac{1}{V_0} \int_{V_0} \chi_k \nabla \cdot \Psi dV = -\langle \nabla \cdot \Psi \rangle_k. \quad (1.56)$$

This implies that  $\nabla \cdot \langle \Psi \rangle_k = 0$ .

By taking the volume averaging to (1.20), we have

$$\partial_t(r_k \rho_k) + \nabla \cdot (r_k \rho_k \langle \mathbf{u}_k \rangle_k^{(k)}) = \Gamma_k, \quad (1.57)$$

where

$$\Gamma_k = -\frac{1}{V_0} \int_{A_k} \rho_k (\mathbf{u}_k - \mathbf{w}_k) \cdot \mathbf{n}_k dA.$$

The interfacial terms  $\Gamma_k$  satisfy the conservation

$$\sum_k \Gamma_k = 0. \quad (1.58)$$

For averaged equations of motion, we have

$$\begin{aligned} \partial_t(r_k \rho_k \langle \mathbf{u}_k \rangle_k^{(k)}) + \nabla \cdot (r_k \rho_k \langle \mathbf{u}_k \rangle_k^{(k)} \otimes \langle \mathbf{u}_k \rangle_k^{(k)}) &= -\nabla(r_k \langle p_k \rangle_k^{(k)}) \\ + \nabla \cdot (\langle \boldsymbol{\tau}_k \rangle_k + \langle \boldsymbol{\tau}_k^T \rangle_k) + \mathbf{M}_k + r_k \langle \mathbf{f}_k \rangle_k^{(k)}, \end{aligned} \quad (1.59)$$

where

$$\mathbf{M}_k = -\frac{1}{V_0} \int_{A_k} \rho_k \mathbf{u}_k (\mathbf{u}_k - \mathbf{w}_k) \cdot \mathbf{n}_k dA + \frac{1}{V_0} \int_{A_k} (\boldsymbol{\tau}_k - pI) \cdot \mathbf{n}_k dA$$

and

$$\langle \boldsymbol{\tau}_k^T \rangle = -\langle \rho_k \hat{\mathbf{u}}_k \otimes \hat{\mathbf{u}}_k \rangle, \quad \hat{\mathbf{u}}_k = (\mathbf{u}_k - \langle \mathbf{u}_k \rangle_k^{(k)}) \chi_k.$$

Since the sum of internal forces is zero, we have the interfacial balance condition

$$\sum_k \mathbf{M}_k + \mathbf{M}_i = 0. \quad (1.60)$$

In the above,  $\mathbf{M}_i$  is the surfacial force such that

$$\mathbf{M}_i = \frac{1}{V_0} \int_{A_i} \sigma \kappa \mathbf{n}_i dA,$$

where  $A_i$  the collection of all the interfaces,  $\sigma$  the surface tension,  $\kappa$  the curvature, and  $\mathbf{n}_i$  the outer normal on the interface.

**Remark 1.3.3** If there are only two phases (say phase 1 and phase 2) in the physical domain of interest, then we have

$$\mathbf{M}_i = \frac{1}{V_0} \int_{A_i} \sigma \kappa \mathbf{n}_i dA = -\sigma \bar{\kappa} \nabla r_1, \quad (1.61)$$

where  $\bar{\kappa}$  is the mean curvature. The above relation can be obtained by the constitutive relation

$$r_1 + r_2 = 1, \quad A_1 = A_2 = A_i \quad (1.62)$$

### 1.3.4 Advection-diffusion in an electrolyte

The species transport is the core issue for studying the electroless plating process. We recall that for a concentration profile  $c_j$  of species  $j$ , the general mass conservation equation can be expressed as

$$\partial_t c_j + \nabla \cdot \mathbf{J}_j = R_j, \quad (1.63)$$

where  $\mathbf{J}_j$  is the overall flux and  $R_j$  is the source or sink of  $c_j$ . If advection and diffusion are considered in the system, then there are two sources for  $J_j$ . First, the advective flux can be expressed as

$$\mathbf{J}_{j,adv} = \mathbf{u}c_j, \quad (1.64)$$

where  $\mathbf{u}$  is the velocity field. Second, the diffusive flux can be approximated by the Fick's first law

$$\mathbf{J}_{j,diff} = -D_j \nabla c_j, \quad (1.65)$$

where  $D_j$  is the diffusion coefficient. Given that the total sum is the summation of these sources, we have

$$\mathbf{J}_j = \mathbf{J}_{j,adv} + \mathbf{J}_{j,diff} = \mathbf{u}c_j - D_j \nabla c_j. \quad (1.66)$$

Therefore, the advection-diffusion equation can be expressed as

$$\partial_t c_j + \nabla \cdot (\mathbf{u}c_j) - \nabla \cdot (D_j \nabla c_j) = R_j. \quad (1.67)$$





## Chapter 2

# Single phase problem

### 2.1 Introduction

In this chapter, the mathematical analysis of the two or three-dimensional electroless plating problem neglecting the gas generation is investigated. For numerical simulation, multi-dimensional electroless processes in geometrically varying micro- or nano-fluidic channels remain computationally expensive so we have investigated on bidimensional cases.

We consider a single chemical species in the electrolyte. The flux of the chemical species on the reacting surface is described in terms of the exchange current. In our case, the exchange current  $I_0$  is given by the Butler-Volmer equation (see for example [74, 95]); it is a linear function of the electrolyte concentration  $c$

$$I_0 = i_0 c := A \left[ \exp \left( \frac{\alpha_0 z F \xi}{R \theta} \right) - \exp \left( \frac{-\beta_0 z F \xi}{R \theta} \right) \right] c, \quad (2.1)$$

where  $A, \alpha_0, \beta_0$  are physical constants,  $R$  is the perfect gas constant,  $F$  the Faraday constant and  $z$  the atomic number of the electrolyte;  $\theta$  is the temperature, and  $\xi$  is the excess potential related to the interaction with other chemical species which, for our purpose is constant [66, 100]. The temperature is also assumed uniform and constant.

The plating occurs on a boundary  $S(t)$  of the electrolyte, causing this interface to move inward the fluid domain but this motion is small because it is only due to plating. The plating being proportional to the concentration  $c$ , the velocity of  $S(t)$  is normal to itself and given by a linear law

$$\mathbf{u} = -\alpha i_0 c \mathbf{n}$$

and  $\alpha$  is small. On the other hand the flux of metal ion through  $S(t)$  is proportional to  $c$

$$D \frac{\partial c}{\partial \mathbf{n}} = -i_0 c$$

where  $D$  is a diffusion constant.

The concentration of the chemical species  $c$  satisfies a convection diffusion equation while the electrolyte flow is modelled by the Navier-Stokes equations.

In order to analyse this coupled problem, we approximate the small displacement of the reaction surface  $S(t)$  by a transpiration approximation [97, 103] on a fixed mean surface  $S$ . It

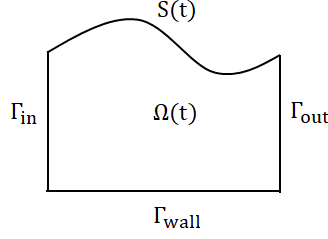


Figure 2.1: The physical domain is the domain occupied by the flow  $\Omega(t)$ ; the chemical deposit is above the free boundary  $S(t)$ . The chemicals flow from the left boundary,  $\Gamma_{in}$ , to the right  $\Gamma_{out}$ . The bottom  $\Gamma_{wall}$  is a solid wall.

leads to an integro-differential condition on  $S$ :

$$-D \frac{\partial c}{\partial n} + i_0 c \left( 1 + \frac{\alpha i_0^2}{D} \int_0^t c(s) ds \right) = 0. \quad (2.2)$$

The mathematical analysis of the Navier-Stokes equations coupled with a convection-diffusion equation for  $c$  is somewhat problematic because of the non-homogenous condition on  $S$  for the velocity. So we restrict the study to the existence of the weak solution to the convection-diffusion equation with a given fluid velocity  $\mathbf{u}$  and even this study is not straightforward. First a time-discretized approximation is shown to have a unique solution using a version of Minty-Browder's theorem and the maximum principle to prove that  $0 \leq c \leq 1$ . The solution of the time continuous problem is obtained as the weak limit of the of the solution of the time-discretized solutions. Some numerical tests are given to justify the transpiration approximation and the convergence of the backward Euler nonlinear scheme.

## 2.2 Modeling of the physical system

The plating chemicals flow in a thin channel between a top and a bottom plate. Due to an electro-potential applied between the two plates the chemicals will deposit on the top plate. Hence the depth of the channel varies with time. A vertical cross section of the 3D system is depicted in Figure 2.1.

### 2.2.1 The fluid flow

The geometry of the fluid part is a two or three-dimensional domain  $\Omega(t)$  bounded on the left by an inflow boundary  $\Gamma_{in}$ , on the right by an outflow boundary  $\Gamma_{out}$ , on the bottom by a flat wall  $\Gamma_{wall}$  and on the top by a time dependent boundary  $S(t)$ . In the three-dimensional case, the remaining boundaries are assumed to be walls. The fluid is viscous, Newtonian and incompressible, so the flow is governed by the Navier-Stokes equations for the velocity  $\mathbf{u}(\mathbf{x}, t)$  and pressure  $p(\mathbf{x}, t)$ :

$$\partial_t \mathbf{u} + \mathbf{u} \cdot \nabla \mathbf{u} - \nu \Delta \mathbf{u} + \nabla p = 0, \quad \nabla \cdot \mathbf{u} = 0, \quad \forall \mathbf{x} \in \Omega(t), \quad \forall t \in [0, T], \quad (2.3)$$

where  $\nu$  is the (constant) kinematic viscosity of the fluid. The initial velocity is given and denoted by  $\mathbf{u}_0$ ; the inflow velocity  $\mathbf{u}_{in}$  is also given on  $\Gamma_{in}$ ; a no slip condition holds on  $\Gamma_{wall} \cup S(t)$ , and

we impose a traction-free outflow condition at  $\Gamma_{out}$ . So at all  $t \in [0, T]$  we have:

$$\mathbf{u} = \mathbf{u}_{in} \text{ on } \Gamma_{in}, \quad \mathbf{u} = 0 \text{ on } \Gamma_{wall}, \quad -\nu \frac{\partial \mathbf{u}}{\partial n} + p\mathbf{n} = 0 \text{ on } \Gamma_{out}. \quad (2.4)$$

We assume that there is no back-flow on  $\Gamma_{out}$ :  $\mathbf{u} \cdot \mathbf{n} \geq 0$ .

**Remark 2.2.1** In general, the traction-free boundary condition on  $\Gamma_{out}$ ,  $-\nu \frac{\partial \mathbf{u}}{\partial n} + p\mathbf{n} = 0$  does not imply  $\mathbf{u} \cdot \mathbf{n} \geq 0$ . However, for electroless plating process, the fluid velocity field near the outlet is near to a Poiseuille flow. We note that the Poiseuille flow in a fixed cross section domain satisfies  $\mathbf{u} \cdot \mathbf{n} \geq 0$  on  $\Gamma_{out}$  and the traction-free condition. For mathematical convenience, the assumption:  $\mathbf{u} \cdot \mathbf{n} \geq 0$  on  $\Gamma_{out}$  is made.

### 2.2.2 The metal ion concentration

The metal ion concentration  $c(\mathbf{x}, t)$  solves a convection-diffusion equation

$$\partial_t c + \mathbf{u} \cdot \nabla c - D\Delta c = 0, \quad \forall \mathbf{x} \in \Omega(t), \quad \forall t \in [0, T] \quad (2.5)$$

with given initial concentration  $c_0$ ;  $D$  is the diffusion constant. The concentration is given on  $\Gamma_{in}$  and a no-flux condition holds on  $\Gamma_{wall}$  and  $\Gamma_{out}$ :

$$c = c_{in} \text{ on } \Gamma_{in}, \quad \frac{\partial c}{\partial n} = 0 \text{ on } \Gamma_{wall} \cup \Gamma_{out}. \quad (2.6)$$

On  $S(t)$  a reaction condition is written as suggested in [66, 100],

$$-D \frac{\partial c}{\partial n} = i_0 c, \quad \mathbf{u} = -\alpha i_0 c \mathbf{n}, \quad \forall x \in S(t), \quad (2.7)$$

where  $i_0$  and  $\alpha$  are constants. Most important for our study:  $\alpha$  is small.

It is also important to remember that  $c$ , being a concentration it must be non-negative and less or equal to one. In particular  $c_0$  and  $c_{in}$  must be chosen in  $[0, 1]$ .

### 2.2.3 The case $\alpha = 0$

When  $\alpha = 0$ , there is no free boundary; consider the case  $\Omega = (0, L) \times (0, 1)$ . With appropriate initial and inflow conditions, the fluid velocity is

$$\mathbf{u} = (u_1, u_2)^T, \quad u_1 = y(1 - y), \quad u_2 = 0$$

Similarly, with appropriate initial and inflow conditions, the concentration depends only on time  $t$  and  $y := x_2$  and solves

$$\partial_t c - D\partial_{yy}c = 0, \quad -D\partial_y c = i_0 c \text{ at } y = 1, \quad \partial_y c = 0 \text{ at } y = 0.$$

It has a closed solution  $c = e^{-D\lambda^2 t} \cos(\lambda y)$  provided  $\lambda$  satisfies:  $\lambda \tan \lambda = \frac{i_0}{D}$ .

When  $0 < \alpha \ll 1$ ,  $\mathbf{u}_{in} = (y(1 - y), 0)^T$ ,  $c_{in} = e^{-D\lambda^2 t} \cos(\lambda y)$ ,  $\mathbf{u}_0 = \mathbf{u}_{in}$ ,  $c_0 = c_{in}|_{t=0}$ , the solution will be a linear perturbation of the above.

### 2.2.4 Transpiration approximation

Experimental observation show that the evolution of  $S(t)$  is small. Following [97, 103], we approximate (2.7) with a transpiration approximation as follows.

Let  $S$  be the initial position of  $S(t)$  and let  $\eta$  be the distance between  $S(t)$  and  $S$  normally to  $S$ , i.e.

$$S(t) = \{\mathbf{x} + \eta(\mathbf{x}, t)\mathbf{n}(\mathbf{x}) : \mathbf{x} \in S\}, \quad \eta(0) = 0$$

where  $\eta(0) = 0$  is short for  $\eta(\mathbf{x}, 0) = 0$  for all  $\mathbf{x} \in S$ . If the radius of curvature of  $S(t)$  and the derivative of  $\eta$  along  $S$  are not large it can be shown that the difference between the normals of  $S$  and  $S(t)$  is second order in  $\eta$  (see [97]). By definition of  $\mathbf{u}$  and by the second equation in (2.7),

$$\frac{d\eta}{dt} = \mathbf{u} \cdot \mathbf{n} = -\alpha i_0 c, \quad \eta(0) = 0, \Rightarrow \eta(t) = -\alpha i_0 \int_0^t c(s) ds. \quad (2.8)$$

By a Taylor expansion, the first equation in (2.7) can be written on  $S$  rather than  $S(t)$ :

$$\begin{aligned} -D \frac{\partial c}{\partial n}(\mathbf{x} + \eta(\mathbf{x}, t)\mathbf{n}(\mathbf{x}), t) &= -D \left( \frac{\partial c}{\partial n}(\mathbf{x}, t) + \eta(\mathbf{x}, t) \frac{\partial^2 c}{\partial n^2}(\mathbf{x}, t) \right) + o(\eta) \\ &= i_0 c(\mathbf{x} + \eta(\mathbf{x}, t)\mathbf{n}(\mathbf{x}), t) = i_0 \left( c(\mathbf{x}, t) + \eta(\mathbf{x}, t) \frac{\partial c}{\partial n}(\mathbf{x}, t) \right) + o(\eta). \end{aligned} \quad (2.9)$$

By (2.8), it is rewritten as

$$-D \left( 1 - \alpha \frac{i_0^2}{D} \int_0^t c(s) ds \right) \frac{\partial c}{\partial n}(\mathbf{x}, t) - i_0 c(\mathbf{x}, t) = \eta(\mathbf{x}, t) D \frac{\partial^2 c}{\partial n^2}(\mathbf{x}, t) + o(\eta) = O(\eta). \quad (2.10)$$

A first order in  $\alpha$  approximation of this condition is

$$-D \frac{\partial c}{\partial n}(\mathbf{x}, t) - i_0 c(\mathbf{x}, t) = 0 \quad (2.11)$$

Neglecting  $o(\eta)$  and using  $\frac{1}{1-y} \approx 1+y$  and neglecting  $D \frac{\partial^2 c}{\partial n^2}$  leads to

$$D \frac{\partial c}{\partial n} + i_0 c \left( 1 + \frac{\alpha i_0^2}{D} \int_0^t c(s) ds \right) = 0 \quad \text{on } S. \quad (2.12)$$

In the discussion below we argue in favor of this approximation where  $\eta D \frac{\partial^2 c}{\partial n^2}$  is neglected.

The second equation of (2.7) is simply written on  $S$  instead of  $S(t)$ . Indeed a similar Taylor expansion shows that

$$\mathbf{u} + \eta \frac{\partial \mathbf{u}}{\partial n} = -\alpha i_0 \left( c + \eta \frac{\partial c}{\partial n} \right) \mathbf{n} + o(\eta \alpha), \quad (2.13)$$

The second equation in (2.7) implies that  $\mathbf{u}$  is  $O(\alpha)$ ; so when all normal derivatives are bounded

$$\mathbf{u} = -\alpha i_0 c \mathbf{n} + O(\eta \alpha), \quad \text{on } S \quad (2.14)$$

### 2.2.5 The final Problem (P)

The domain and the top boundary are now fixed and denoted by  $\Omega$  and  $S$ ; the boundary of  $\Omega$  is

$$\Gamma := \partial\Omega = \Gamma_{in} \cup \Gamma_{wall} \cup \Gamma_{out} \cup S.$$

We propose to solve (2.3) and (2.5) in  $\Omega \times (0, T)$  subject to initial conditions and boundary conditions (2.4) and (2.6) and

$$D \frac{\partial c}{\partial n} + \left(1 + \frac{\alpha i_0^2}{D} \int_0^t c(s) ds\right) i_0 c = 0 \quad \text{on } S, \quad (2.15)$$

$$\mathbf{u} = -\alpha i_0 c \mathbf{n} \quad \text{on } S. \quad (2.16)$$

### 2.2.6 Discussion:

If we had kept the term  $\eta(\mathbf{x}, t) D \frac{\partial^2 c}{\partial n^2}(\mathbf{x}, t)$  in (2.12), this condition would have been second order. But even without it we expect it to be near second order when  $c$  varies slowly and  $\Omega$  is elongated, because (2.5) will not be far from  $-D \frac{\partial^2 c}{\partial n^2} \approx 0$ .

One of the purpose of this article is to analyse the additional nonlinear term in (2.15). In the numerical section, it will be compared to the first order condition obtained by setting  $\alpha = 0$  in (2.15).

A third condition can be obtained as follows. If  $s$  denotes arc length on  $S$ , the PDE which governs  $c$  tells us that near  $S$

$$\partial_t c + \mathbf{u} \cdot \mathbf{n} \frac{\partial c}{\partial n} = D \frac{\partial^2 c}{\partial n^2} + D \frac{\partial^2 c}{\partial s^2}$$

Assuming that the variations in  $s$  are much smaller than those in  $n$ , we obtain

$$D \frac{\partial^2 c}{\partial n^2} = \partial_t c - \alpha i_0 c \frac{\partial c}{\partial n} = \partial_t c + O(\alpha). \quad (2.17)$$

Inserting the above equation into (2.10), we get

$$-D \left(1 - \alpha \frac{i_0^2}{D} \int_0^t c(s) ds\right) \frac{\partial c}{\partial n}(\mathbf{x}, t) - i_0 c(\mathbf{x}, t) = - \left(\alpha i_0 \int_0^t c(s) ds\right) (\partial_t c + O(\alpha)). \quad (2.18)$$

As for getting (2.12), by a first order approximation ( $\frac{1}{1-y} \approx 1+y$ ) and a discard of the term of order  $O(\alpha^2)$ , leads to

$$D \frac{\partial c}{\partial n} + i_0 c + \alpha i_0 \left(\frac{i_0^2}{D} c - \partial_t c\right) \int_0^t c(s) ds = 0 \quad \text{on } S. \quad (2.19)$$

### 2.2.7 Plan

If it wasn't for the boundary conditions, the mathematical analysis of (2.3), (2.5), and (2.11), (2.16) is somewhat classical, so we shall focus on the problem raised by the nonlinear boundary conditions (2.3), (2.5), (2.15), (2.16). Then, at the end we shall argue that there is no essential new difficulty if the term  $\partial_t c$  is added, namely problem (2.3), (2.5), (2.19), (2.16).

Once more, existence of  $c$  will be shown for a given flow  $\mathbf{u}, p$ . The coupled problem is analysed only in the numerical section.

## 2.3 Variational formulation

### 2.3.1 Notations

For convenience,  $C$ ,  $C'$  and  $C_i$ ,  $i = 1, 2, 3, \dots$ , denote generic constants independent of  $\mathbf{u}$  and  $c$ . We denote  $d = 2, 3$  the dimension.

We use the standard notations:  $f^+ = \max\{f, 0\}$  and  $f^- = -\min\{f, 0\}$ .

We denote by  $\|\cdot\|_s$  the norm of  $H^s(\Omega)$  and by  $\|\cdot\|_{s,\Gamma}$  the norm of  $H^s(\Gamma)$  for  $\Gamma \subset \partial\Omega$ .

If  $B$  is a Banach space,  $B'$  denotes its dual space. The  $L^2(\Omega)$  inner product is  $(\cdot, \cdot)$  and the duality product between  $B$  and  $B'$  is  $\langle \cdot, \cdot \rangle_{B, B'}$ .

We define

$$W = \{w \in H^1(\Omega) : w|_{\Gamma_{in}} = 0\};$$

since  $W$  is closed in  $H^1(\Omega)$  and  $H^1(\Omega)$  is a Hilbert space, then so is  $W$ .

We assume that  $\mathbf{u} \in L^2(0, T; \mathbf{V}_{div}) \cap L^\infty(0, T; L^2(\Omega)^d)$  is given, where

$$\mathbf{V}_{div} := \{\mathbf{v} \in H^1(\Omega)^d : \nabla \cdot \mathbf{v} = 0\}.$$

In view of (2.16) with nonnegative concentration  $c$  and assuming that there is no back-flow on  $\Gamma_{out}$ , we make the following assumptions for  $\mathbf{u}$ :

$$\begin{aligned} \text{(U1)} \quad & \mathbf{u} \cdot \mathbf{n} \leq 0 \quad \text{on } S, \\ \text{(U2)} \quad & \mathbf{u} \cdot \mathbf{n} \geq 0 \quad \text{on } \Gamma_{out}. \end{aligned} \tag{2.20}$$

In variational form (2.5), (2.6), (2.15) is: Let  $w(x, t)$  be a sufficiently smooth function defined in  $\Omega \times [0, T]$  and vanishing on  $\Gamma_{in}$ . Multiplying  $w(x, t)$  with (2.5), integrating over  $\Omega$ , and using (2.6), (2.15), (2.16), we have

$$\begin{aligned} & \int_{\Omega} (\partial_t c + \mathbf{u} \cdot \nabla c - D \Delta c) w dx \\ &= \int_{\Omega} (\partial_t c) w dx + \frac{1}{2} \int_{\Omega} (\mathbf{u} \cdot \nabla c) w dx - \frac{1}{2} \int_{\Omega} (\mathbf{u} \cdot \nabla w) c dx + \frac{1}{2} \int_{\partial\Omega} (\mathbf{u} \cdot \mathbf{n}) c w \\ &+ \int_{\Omega} D \nabla c \cdot \nabla w dx - \int_{\partial\Omega} D \frac{\partial c}{\partial n} w \\ &= \int_{\Omega} (\partial_t c) w dx + \frac{1}{2} \int_{\Omega} [(\mathbf{u} \cdot \nabla c) w - (\mathbf{u} \cdot \nabla w) c] dx + \int_{\Omega} D \nabla c \cdot \nabla w dx \\ &+ \frac{1}{2} \int_{\Gamma_{out}} (\mathbf{u} \cdot \mathbf{n}) c w + \int_S \left(1 - \frac{\alpha c}{2} + \frac{\alpha i_0^2}{D} \int_0^t c(s) ds\right) i_0 c w. \end{aligned} \tag{2.21}$$

The resulting variational formulation reads:

#### Problem (P)

Given  $c_0 \in H^1(\Omega)$ ,  $c_0(x) \in [0, 1]$ ,  $c_{in} \in H^{1/2}(\Gamma_{in})$ ,  $c_{in}(x) \in [0, 1]$ , and  $\mathbf{u} \in L^2(0, T; \mathbf{V}_{div})$  satisfying (U1), (U2), find  $c \in L^2(0, T; H^1(\Omega))$   $\partial_t c \in L^2(0, T; W')$ , such that,  $c(0) = c_0$ ,  $c|_{\Gamma_{in}} = c_{in}$  and, for all  $w \in W$ ,

$$\begin{aligned} & \langle \partial_t c, w \rangle_{W', W} + \int_{\Omega} D \nabla c \cdot \nabla w dx + \frac{1}{2} \int_{\Omega} [(\mathbf{u} \cdot \nabla c) w - (\mathbf{u} \cdot \nabla w) c] dx \\ &+ \frac{1}{2} \int_{\Gamma_{out}} (\mathbf{u} \cdot \mathbf{n}) c w + \int_S \left(1 - \frac{\alpha c}{2} + \frac{\alpha i_0^2}{D} \int_0^t c(s) ds\right) i_0 c w = 0. \end{aligned} \tag{2.22}$$

The following result, central to this chapter, shows existence of the concentration profile  $c$  when the velocity field  $\mathbf{u}$ , is known:

**Theorem 2.3.1** Given  $c_0 \in H^1(\Omega)$ ,  $c_0(x) \in [0, 1]$ ,  $c_{in} \in H^{1/2}(\Gamma_{in})$ ,  $c_{in}(x) \in [0, 1]$ , and  $\mathbf{u} \in L^2(0, T; \mathbf{V}_{div})$  satisfying (U1) and (U2), there exists a unique  $c \in L^2(0, T; H^1(\Omega))$  with  $\partial_t c \in L^2(0, T; W')$  such that

$$\begin{aligned} & \int_0^T \langle \partial_t c, w \rangle_{W', W} dt + \frac{1}{2} \left( \int_0^T \int_{\Omega} [(\mathbf{u} \cdot \nabla c)w - (\mathbf{u} \cdot \nabla w)c] dx dt \right) \\ & + D \int_0^T \int_{\Omega} \nabla c \cdot \nabla w dx dt + \int_0^T \int_S \left( 1 - \frac{\alpha c}{2} + \frac{\alpha i_0^2}{D} \int_0^t c(s) ds \right) i_0 c w dt \\ & + \int_0^T \int_S \frac{\alpha i_0^3}{D} c \left( \int_0^t c(s) ds \right) w dt + \frac{1}{2} \int_0^T \int_{\Gamma_{out}} (\mathbf{u} \cdot \mathbf{n}) c w dt \\ & = 0. \end{aligned} \quad (2.23)$$

for all  $w \in L^2(0, T; W)$ , and  $c(0) = c_0 \in H^1(\Omega)$ , and  $c|_{\Gamma_{in}} = c_{in} \in H^{1/2}(\Gamma_{in})$ .

**Remark 2.3.1** The existence and regularity of the coupled problem  $\{\mathbf{u}, c\}$  will not be studied. Mostly because it would require minute and perhaps hard to obtain estimates due to the corners in the domain as in [9, 68, 14], the traction-free boundary condition, etc, but also because,  $\mathbf{u}$  is merely weakly coupled with  $c$  only through the boundary condition on  $S$ . Furthermore, due to the numerical values of the physical constants,  $\mathbf{u}$  is small on  $\Gamma_{in}$ . Therefore, we focus on the solution to the convection-diffusion equation (2.22), for which, as we shall see, the functional setting is not so simple.

### 2.3.2 Convexification

The term  $c - \frac{\alpha c^2}{2}$  in the integral on  $S$  is problematic because it is not monotone so it makes the problem non-coercive. Indeed its primitive  $\psi(c) := \frac{c^2}{2} - \frac{\alpha c^3}{6}$  is nonconvex beyond  $c > \frac{1}{\alpha}$ . But the physics require that  $c \in [0, 1]$  and the maximum principle will insure it. So any modification of  $\psi$  outside  $(0, 1)$  will not affect the solution; hence to work with a convex potential let us replace  $\psi$  by (see Figure 2.2).

$$\Psi(c) = \begin{cases} \frac{c^2}{2} - \frac{\alpha c^3}{6} & \text{if } c < \frac{1}{\alpha}, \\ \frac{1}{2\alpha} - \frac{1}{6\alpha^2} & \text{otherwise.} \end{cases} \quad (2.24)$$

Let  $\rho$  be any time dependent function defined on  $[0, T]$ . We define

$$(\phi(\rho))(t) = i_0 \dot{\Psi}(\rho(t)) + \frac{\alpha i_0^3}{D} \rho(t) \int_0^t |\rho(s)| ds, \quad t \in [0, T], \quad (2.25)$$

where  $\dot{\Psi}(c)$  is the derivative of  $\Psi$  with respect to  $c$ :

$$\dot{\Psi}(c) = \begin{cases} c - \frac{\alpha c^2}{2} & \text{if } c < \frac{1}{\alpha}, \\ \frac{1}{2\alpha} & \text{otherwise.} \end{cases} \quad (2.26)$$



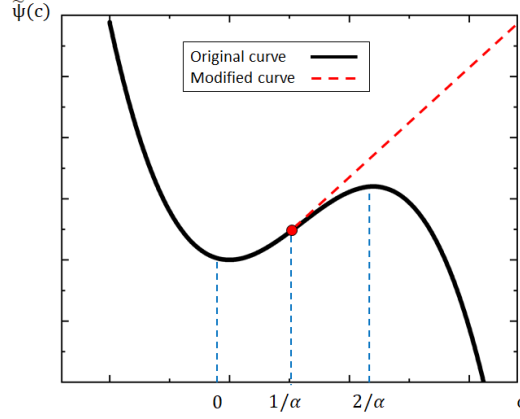


Figure 2.2: Graphic showing the modification of the nonconvex function  $c \mapsto \frac{c^2}{2} - \frac{\alpha c^3}{6}$  into a convex one.

Naturally  $\dot{\Psi}$  is monotone increasing. Note that  $\Psi$  is strictly convex and  $\dot{\Psi}$  is strictly increasing in  $[0, \frac{1}{\alpha}]$ .

The convexified variational formulation replacing (2.22) is

**Problem ( $P_c$ )**

Given  $c_0 \in H^1(\Omega)$ ,  $c_0(x) \in [0, 1]$ ,  $c_{in} \in H^{1/2}(\Gamma_{in})$ ,  $c_{in}(x) \in [0, 1]$ , and  $\mathbf{u} \in L^2(0, T; \mathbf{V}_{div})$  satisfying (U1), (U2), find  $c \in L^2(0, T; H^1(\Omega))$  satisfying  $c|_{\Gamma_{in}} = c_{in} \in H^{1/2}(\Gamma_{in})$ ,  $\partial_t c \in L^2(0, T; W')$ ,  $\phi(c) \in L^2(0, T; L^2(S))$ , and

$$\begin{aligned} \langle \partial_t c, w \rangle_{W', W} + \int_{\Omega} D \nabla c \cdot \nabla w dx + \frac{1}{2} \int_{\Omega} [(\mathbf{u} \cdot \nabla c)w - (\mathbf{u} \cdot \nabla w)c] dx \\ + \frac{1}{2} \int_{\Gamma_{out}} (\mathbf{u} \cdot \mathbf{n})cw + \int_S \phi(c)w = 0, \quad \forall w \in W. \end{aligned} \quad (2.27)$$

Note that when  $0 \leq c \leq 1$ , then both  $c$  and  $\phi(c) \in L^\infty(\Omega \times (0, T))$ .

The proof of existence goes by steps. We assume that  $\mathbf{u} \in L^2(0, T; \mathbf{V}_{div}) \cap L^\infty(0, T; L^2(\Omega)^d)$ , so as to focus on the equation for  $c$  with  $\mathbf{u}$  given. We will first discretize in time, show existence for the time discretized problem and then let the time step tend to zero.

## 2.4 Existence for the time-discretized problem

Let  $N \in \mathbb{N}^+$  and let  $\delta t = \frac{T}{N}$  be the time step.

**Discrete velocity field  $\mathbf{u}$**

Since functions in a Bochner space  $L^p(0, T; X)$  for all Banach space  $(X, \|\cdot\|)$  can be approximated by step functions on a uniform discretization of  $(0, T)$  (see for instance [44, 65]), we define

$\mathbf{u}_\delta : (0, T] \rightarrow \mathbf{V}_{div}$  by

$$\mathbf{u}_\delta(t) = \sum_{m=0}^{N-1} \mathbf{u}^{m+1} \chi_{(m\delta t, (m+1)\delta t]}(t), \quad (2.28)$$

where  $\mathbf{u}^j = \frac{1}{\delta t} \int_{j\delta t}^{(j+1)\delta t} \mathbf{u}(s) ds$  for  $j = 0, \dots, N-1$ . For convenience, we further define  $\mathbf{u}^0 = \mathbf{u}(0) \in \mathbf{V}_{div}$ . Obviously,  $\mathbf{u}^j \in \mathbf{V}_{div}$  for all  $0 \leq j \leq N$ . To show that  $\mathbf{u}_\delta$  converges to  $\mathbf{u}$  strongly in  $L^2(0, T; H^1(\Omega)^d)$ , we need a lemma:

**Lemma 2.4.1** Let  $f \in L^2([a, b])$  for  $a, b \in \mathbb{R}$ ,  $a < b$ , and  $N > 0$  be an integer. Defining  $\delta t = \frac{b-a}{N}$ , we have

$$\delta t \sum_{j=0}^{N-1} \int_{a+j\delta t}^{a+(j+1)\delta t} \int_{a+j\delta t}^{a+(j+1)\delta t} \frac{|f(s) - f(t)|^2}{\delta t^2} ds dt \rightarrow 0, \quad \text{as } \delta t \rightarrow 0 \quad (2.29)$$

*Proof.* Given  $\epsilon_1 > 0$ , there exists  $g \in C([a, b])$  such that

$$\int_a^b |f - g|^2 dt < \epsilon_1$$

We note that choice of  $g$  is independent to  $\delta t$ . With given  $g$  in hand, for every  $\epsilon_2 > 0$ , there exists  $\delta > 0$  such that for every  $s, t \in [a, b]$ , we have

$$|g(s) - g(t)| < \epsilon_2, \quad \text{whenever } |s - t| < \delta.$$

Choosing  $\delta t < \delta$ , we have the estimate:

$$\begin{aligned} & \sum_{j=0}^{N-1} \int_{a+j\delta t}^{a+(j+1)\delta t} \int_{a+j\delta t}^{a+(j+1)\delta t} |f(s) - f(t)|^2 ds dt \\ & \leq 3 \sum_{j=0}^{N-1} \int_{a+j\delta t}^{a+(j+1)\delta t} \int_{a+j\delta t}^{a+(j+1)\delta t} (|f(s) - g(s)|^2 + |g(s) - g(t)|^2 + |f(t) - g(t)|^2) ds dt \\ & \leq 6 \sum_{j=0}^N \delta t \left( \int_{a+j\delta t}^{a+(j+1)\delta t} \int_{a+j\delta t}^{a+(j+1)\delta t} |f(s) - g(s)|^2 ds \right) + 3 \sum_{j=0}^{N-1} \int_{a+j\delta t}^{a+(j+1)\delta t} \int_{a+j\delta t}^{a+(j+1)\delta t} |g(s) - g(t)|^2 ds dt \\ & \leq 6\delta t \epsilon_1 + 3(b-a)\delta t \epsilon_2 \end{aligned} \quad (2.30)$$

Therefore,

$$\delta t \sum_{j=0}^{N-1} \int_{a+j\delta t}^{a+(j+1)\delta t} \int_{a+j\delta t}^{a+(j+1)\delta t} \frac{|f(s) - f(t)|^2}{\delta t^2} ds dt \leq 6\epsilon_1 + 3(b-a)\epsilon_2. \quad (2.31)$$

By the arbitrariness of  $\epsilon_1$  and  $\epsilon_2$ , the proof is completed. Q.E.D.

**Proposition 2.4.1** Let  $\mathbf{u}_\delta$  be defined by (2.28), we have the following:

$$\|\mathbf{u} - \mathbf{u}_\delta\|_{L^2(0, T; H^1(\Omega))} \rightarrow 0 \quad \text{as } \delta t \rightarrow 0. \quad (2.32)$$

*Proof.*

$$\begin{aligned}
& \int_0^T \|\mathbf{u}_\delta(t) - \mathbf{u}(t)\|_1^2 dt \\
&= \sum_{j=0}^{N-1} \int_{j\delta t}^{(j+1)\delta t} \|\mathbf{u}^{j+1} - \mathbf{u}(t)\|_1^2 dt \\
&= \sum_{j=0}^{N-1} \int_{j\delta t}^{(j+1)\delta t} \left\| \frac{1}{\delta t} \int_{j\delta t}^{(j+1)\delta t} (\mathbf{u}(s) - \mathbf{u}(t)) ds \right\|_1^2 dt \\
&\leq \sum_{j=0}^{N-1} \int_{j\delta t}^{(j+1)\delta t} \left( \frac{1}{\delta t} \int_{j\delta t}^{(j+1)\delta t} \|\mathbf{u}(s) - \mathbf{u}(t)\|_1^2 ds \right) dt \\
&= \delta t \sum_{j=0}^{N-1} \int_{j\delta t}^{(j+1)\delta t} \int_{j\delta t}^{(j+1)\delta t} \frac{\|\mathbf{u}(s) - \mathbf{u}(t)\|_1^2}{\delta t^2} ds dt
\end{aligned} \tag{2.33}$$

Defining the function  $f : [0, T] \rightarrow \mathbb{R}$  by  $s \mapsto \|\mathbf{u}(s)\|_1^2$  and applying Lemma 2.4.1, the proof is completed. Q.E.D.

We observe that  $\mathbf{u}_\delta$  is strongly convergent to  $\mathbf{u}$  in  $L^2(0, T; H^1(\Omega)^d)$ . Thus,

**Corollary 2.4.1** There exists a constant  $C$  depending only on  $\Omega, T, \mathbf{u}$  so that

$$\|\mathbf{u}_\delta\|_{L^2(0, T; H^1(\Omega)^d)} \leq C \quad \forall \delta t \geq 0. \tag{2.34}$$

#### Problem ( $P_c^m$ )

For each integer  $m \in (0, N-1)$ , given  $c^m \in H^1(\Omega)$ , and  $\mathbf{u}^{m+1} = \mathbf{u}_\delta((m+1)\delta t)$  satisfying (U1), (U2), find  $c^{m+1} \in H^1(\Omega)$  such that for all  $w \in W$ ,

$$\begin{aligned}
& \int_\Omega \frac{c^{m+1} - c^m}{\delta t} w dx + D \int_\Omega \nabla c^{m+1} \cdot \nabla w dx \\
&+ \frac{1}{2} \int_\Omega [(\mathbf{u}^{m+1} \cdot \nabla c^{m+1})w - (\mathbf{u}^{m+1} \cdot \nabla w)c^{m+1}] dx \\
&+ \int_S \phi_m(c^{m+1})w + \frac{1}{2} \int_{\Gamma_{out}} (\mathbf{u}^{m+1} \cdot \mathbf{n})c^{m+1}w = 0
\end{aligned} \tag{2.35}$$

with  $c^{m+1}|_{\Gamma_{in}} = c_{in} \in H^{1/2}(\Gamma_{out})$ , where  $\phi_m(c^{m+1})$  is the following time approximation of  $\phi(c)$ ,

$$\phi_m(c^{m+1}) = i_0 \dot{\Psi}(c^{m+1}) + \frac{\alpha i_0^3}{D} \left( \sum_{j=0}^m c^j \delta t \right) c^{m+1}.$$

The boundary condition is given by  $c|_{\Gamma_{in}} = c_{in} \in H^{1/2}(\Gamma_{in})$ ,  $0 \leq c_{in} \leq 1$ . The initial value is  $c^0 = c_0$  with  $c_0 \in H^1(\Omega)$ ,  $c_0|_{\Gamma_{in}} = c_{in} \in H^{1/2}(\Gamma_{in})$ ,  $0 \leq c_0 \leq 1$ .

#### 2.4.1 Existence of the solution to the time-discretized Problem ( $P_c^m$ )

To prove the existence, the Minty-Browder Theorem (see Theorem 9.14.1 in [27] and a series of works by Minty and Browder[83, 84, 21]) will be used.

**Theorem 2.4.1 (Minty-Browder)** Let  $B$  be a reflexive Banach space and  $\|\cdot\|$  its norm. Let  $A : B \rightarrow B'$  a continuous mapping such that

- (i)  $\langle Au - Av, u - v \rangle > 0 \quad \forall u, v \in B, \quad u \neq v$
- (ii)  $\lim_{\|u\| \rightarrow \infty} \|u\|^{-1} \langle Au, u \rangle = +\infty$ .

Then, for any  $b \in B'$ , there is a unique  $u$  such that  $Au = b$ .

**Remark 2.4.1** The continuity of  $A$  in Theorem 2.4.1 can be generalized to hemicontinuity, or demicontinuity.

The theorem will be applied to  $c^m - \tilde{c}_{in}$  where  $\tilde{c}_{in} \in H^1(\Omega)$  is a lift of the boundary conditions defined as the unique solution of

$$\int_{\Omega} D \nabla \tilde{c}_{in} \cdot \nabla w dx = 0, \quad \forall w \in W \quad (2.36)$$

such that  $\tilde{c}_{in} = c_{in}$  on  $\Gamma_{in}$ . With  $c_{in} \in H^{1/2}(\Gamma_{in})$ , the existence and uniqueness of  $\tilde{c}_{in}$  can be guaranteed (see Section 7 in [99]).

**Lemma 2.4.2** If  $0 \leq c_{in} \leq 1$ , then  $\tilde{c}_{in}$  satisfies  $0 \leq \tilde{c}_{in} \leq 1$  a.e.

*Proof.* The argument is classical; let us recall it for the reader's convenience. Note that  $(\tilde{c}_{in} - 1)^+$  and  $(\tilde{c}_{in})^-$  belong to  $W$ . Choosing  $w = (\tilde{c}_{in})^-$  in (2.36), gives  $\|\nabla(\tilde{c}_{in})^-\|_0^2 = 0$ . Hence  $(\tilde{c}_{in})^- = 0$  i.e.  $\tilde{c}_{in} \geq 0$ .

Now choosing  $w = (\tilde{c}_{in} - 1)^+$  in (2.36) implies  $\|\nabla(\tilde{c}_{in} - 1)^+\|_0^2 = 0$ . Hence  $(\tilde{c}_{in} - 1)^+ = 0$ , i.e.  $\tilde{c}_{in} \leq 1$  a.e. in  $\Omega$ . Q.E.D.

**Proposition 2.4.2** Let  $m \geq 0$ . If  $0 \leq c^j \leq 1$  a.e. in  $\Omega$ ,  $c^j \in H^1(\Omega)$  for all  $j \leq m$ , then  $c^{m+1} \in H^1(\Omega)$  and  $0 \leq c^{m+1} \leq 1$  a.e. in  $\Omega$ .

*Proof.* Letting  $w = (c^{m+1})^-$  in (2.35), gives

$$\begin{aligned} & -\frac{1}{\delta t} \|(c^{m+1})^-\|_0^2 - D \|\nabla(c^{m+1})^-\|_0^2 - \frac{1}{2} \int_{\Gamma_{out}} (\mathbf{u}^{m+1} \cdot \mathbf{n})(c^{m+1})^{-2} \\ & + \int_S i_0 \dot{\Psi}(c^{m+1})(c^{m+1})^- - \frac{\alpha i_0^3}{D} \sum_{j=0}^m c^j \delta t (c^{m+1})^{-2} = \frac{1}{\delta t} \int_{\Omega} c^m (c^{m+1})^- \geq 0 \end{aligned} \quad (2.37)$$

All terms on the left are obviously negative except  $\dot{\Psi}(c^{m+1})(c^{m+1})^-$ . Two cases: if  $c \geq \frac{1}{\alpha}$  then  $c^- = 0$  and  $\dot{\Psi}(c)c^- = 0$ ; if  $c < \frac{1}{\alpha}$  then  $\dot{\Psi}(c)c^- = (c - \frac{\alpha}{2}c^2)c^- = -(c^-)^2 - \frac{\alpha}{2}c^2c^- \leq 0$ . Hence  $\dot{\Psi}(c^{m+1})(c^{m+1})^- \leq 0$  always; thus (2.37) leads to  $\|(c^{m+1})^-\|_0^2 = 0$ .

Define  $\bar{c}^{m+1} = c^{m+1} - 1$ . It satisfies

$$\begin{aligned} & \int_{\Omega} \frac{\bar{c}^{m+1} - \bar{c}^m}{\delta t} w + \int_{\Omega} D \nabla \bar{c}^{m+1} \cdot \nabla w dx \\ & + \frac{1}{2} \int_{\Omega} [(\mathbf{u}^{m+1} \cdot \nabla \bar{c}^{m+1})w - (\mathbf{u}^{m+1} \cdot \nabla w)\bar{c}^{m+1}] dx \\ & - \frac{1}{2} \int_{S \cup \Gamma_{out}} (\mathbf{u}^{m+1} \cdot \mathbf{n})w + \int_S i_0 \dot{\Psi}(c^{m+1})w + \int_S \frac{\alpha i_0^3}{D} \sum_{j=0}^m c^j \delta t c^{m+1} w \\ & + \frac{1}{2} \int_{\Gamma_{out}} (\mathbf{u}^{m+1} \cdot \mathbf{n})(\bar{c}^{m+1} + 1)w = 0 \end{aligned} \quad (2.38)$$

Testing with  $w = (\bar{c}^{m+1})^+$ , gives

$$\begin{aligned} & \frac{1}{\delta t} \|(\bar{c}^{m+1})^+\|_0^2 - \frac{1}{\delta t} \int_{\Omega} \bar{c}^m (\bar{c}^{m+1})^+ + D \|\nabla(\bar{c}^{m+1})^+\|_0^2 - \frac{1}{2} \int_S (\mathbf{u}^{m+1} \cdot \mathbf{n}) (\bar{c}^{m+1})^+ \\ & \int_S i_0 \dot{\Psi}(c^{m+1}) (\bar{c}^{m+1})^+ + \frac{\alpha i_0^3}{D} \int_S \sum_{j=0}^m c^j \delta t c^{m+1} (\bar{c}^{m+1})^+ \\ & + \frac{1}{2} \int_{\Gamma_{out}} (\mathbf{u}^{m+1} \cdot \mathbf{n}) ((\bar{c}^{m+1})^+ + 1) (\bar{c}^{m+1})^+ = 0. \end{aligned} \quad (2.39)$$

By the induction hypothesis,  $\bar{c}^m$  is negative; observe that  $\mathbf{u}^{m+1} \cdot \mathbf{n} \leq 0$  on  $S$  by (U1),  $\mathbf{u}^{m+1} \cdot \mathbf{n} \geq 0$  on  $\Gamma_{out}$  by (U2) and  $\dot{\Psi}(c^{m+1}) \geq 0$  because  $c^{m+1} \geq 0$ . So we have that  $\|(\bar{c}^{m+1})^+\|_0^2 = 0$ . Q.E.D.

Let us define

$$\tilde{c}^m := c^m - \tilde{c}_{in} \in W, \quad m = 0, 1, \dots, N.$$

**Remark 2.4.2** As  $\tilde{c}^m \in [-1, 1]$  and  $\dot{\Psi}(c^m) \in [0, 1]$ , therefore  $|\dot{\Psi}(c^m) \tilde{c}^m| \leq 1$ .

By construction, (2.35), which defines Problem  $P_c^m$ , can be rewritten as

**Problem ( $\tilde{P}_c^m$ )**

For each integer  $m \in (0, N-1)$ , given  $\tilde{c}^m \in H^1(\Omega)$ ,  $\tilde{c}_{in} \in H^1(\Omega)$ ,  $\tilde{c}_{in}(x) \in [0, 1]$ , and  $\mathbf{u}^{m+1} = \mathbf{u}_{\delta}((m+1)\delta t)$  satisfying (U1), (U2), find  $\tilde{c}^{m+1} \in W$  such that for all  $w \in W$ ,

$$\begin{aligned} & \frac{1}{\delta t} \int_{\Omega} \tilde{c}^{m+1} w dx + \frac{1}{2} \int_{\Omega} [(\mathbf{u}^{m+1} \cdot \nabla \tilde{c}^{m+1}) w - (\mathbf{u}^{m+1} \cdot \nabla w) \tilde{c}^{m+1}] dx \\ & + D \int_{\Omega} \nabla \tilde{c}^{m+1} \cdot \nabla w dx + \int_S \phi_m(c^{m+1}) w + \frac{1}{2} \int_{\Gamma_{out}} (\mathbf{u}^{m+1} \cdot \mathbf{n}) \tilde{c}^{m+1} w \\ & = -\frac{1}{2} \int_{\Omega} [(\mathbf{u}^{m+1} \cdot \nabla \tilde{c}_{in}) w - (\mathbf{u}^{m+1} \cdot \nabla w) \tilde{c}_{in}] dx + \frac{1}{\delta t} \int_{\Omega} \tilde{c}^m w dx - \frac{1}{2} \int_{\Gamma_{out}} (\mathbf{u}^{m+1} \cdot \mathbf{n}) \tilde{c}_{in} w \end{aligned} \quad (2.40)$$

Now define the mapping  $A : W \rightarrow W'$  by

$$\begin{aligned} \langle A\rho, w \rangle &= \frac{1}{\delta t} \int_{\Omega} \rho w dx + \frac{1}{2} \int_{\Omega} [(\mathbf{u}^{m+1} \cdot \nabla \rho) w - (\mathbf{u}^{m+1} \cdot \nabla w) \rho] dx \\ & + D \int_{\Omega} \nabla \rho \cdot \nabla w dx + \int_S \phi_m(\rho + \tilde{c}_{in}) w + \frac{1}{2} \int_{\Gamma_{out}} (\mathbf{u}^{m+1} \cdot \mathbf{n}) \rho w \end{aligned} \quad (2.41)$$

Since  $W$  is closed in  $H^1(\Omega)$  and  $H^1(\Omega)$  is a Hilbert space, then so is  $W$ .

**Lemma 2.4.3** Let  $m \geq 0$ . We suppose that  $c_j \in H^1(\Omega)$  for all  $j \leq m$ , then  $A : W \rightarrow W'$  defined by (2.41) is locally Lipschitz continuous.

The proof is fairly straightforward but long, so it is postponed to Appendix A so as not to break the thread of the proof of existence of  $(P_c^m)$ . From the definition of  $A$  by (2.41), there is no essential difficulty to arrive, via a sequence of inequalities, at

$$\begin{aligned} & |\langle A\rho_1 - A\rho_2, w \rangle| \\ & \leq \left( C_1 + C_2 \|\mathbf{u}^{m+1}\|_1 + C_3(\|\rho_1\|_1 + \|\rho_2\|_1) + C_4 \delta t \sum_{j=0}^m \|c^j\|_1 \right) \|\rho_1 - \rho_2\|_1 \|w\|_1, \end{aligned} \quad (2.42)$$

**Lemma 2.4.4** Let  $\rho_1, \rho_2, \rho \in W$  and  $m \geq 0$ . We suppose that  $0 \leq c^j \leq 1$  a.e. in  $\Omega$  for all  $j \leq m$ .  $A : W \rightarrow W'$  defined by (2.41) satisfies

- (i)  $\langle A\rho_1 - A\rho_2, \rho_1 - \rho_2 \rangle > 0$  if  $\rho_1 \neq \rho_2$
- (ii)  $\lim_{\|\rho\|_1 \rightarrow +\infty} \|\rho\|_1^{-1} \langle A\rho, \rho \rangle = +\infty$ .

*Proof.* To show (i), we use (2.41) with  $\rho_1, \rho_2 \in W$ ,

$$\begin{aligned} \langle A\rho_1 - A\rho_2, w \rangle &= \frac{1}{\delta t} \int_{\Omega} (\rho_1 - \rho_2) w dx \\ &+ \frac{1}{2} \int_{\Omega} [(\mathbf{u}^{m+1} \cdot \nabla(\rho_1 - \rho_2))w - (\mathbf{u}^{m+1} \cdot \nabla w)(\rho_1 - \rho_2)] dx + D \int_{\Omega} \nabla(\rho_1 - \rho_2) \cdot \nabla w dx \\ &+ \int_S (\phi_m(\rho_1 + \tilde{c}_{in}) - \phi_m(\rho_2 + \tilde{c}_{in}))w + \frac{1}{2} \int_{\Gamma_{out}} (\mathbf{u}^{m+1} \cdot \mathbf{n})(\rho_1 - \rho_2)w. \end{aligned} \quad (2.43)$$

By the definition of  $\phi_m$ ,  $c^j$  are given for  $j \leq m$  irrespectively of  $\rho$ . Let  $w = \rho_1 - \rho_2$  in the above equation, one obtain

$$\begin{aligned} \langle A\rho_1 - A\rho_2, \rho_1 - \rho_2 \rangle &= \\ &\int_{\Omega} \frac{1}{\delta t} (\rho_1 - \rho_2)^2 dx + D \int_{\Omega} |\nabla(\rho_1 - \rho_2)|^2 dx + \frac{1}{2} \int_{\Gamma_{out}} (\mathbf{u}^{m+1} \cdot \mathbf{n})(\rho_1 - \rho_2)^2 \\ &\int_S \frac{\alpha_0^3}{D} \sum_{j=0}^m c^j \delta t (\rho_1 - \rho_2)^2 + \int_S (\dot{\Psi}(\rho_1 + \tilde{c}_{in}) - \dot{\Psi}(\rho_2 + \tilde{c}_{in}))(\rho_1 - \rho_2). \end{aligned} \quad (2.44)$$

Recall that  $\mathbf{u}^{m+1} \cdot \mathbf{n} \geq 0$  on  $\Gamma_{out}$ . All the terms on the right are obviously positive, except the last one. Without loss of generality, we assume that  $\rho_2 > \rho_1$ ; we know that  $\dot{\Psi}$  is strictly increasing. That is,  $\dot{\Psi}(\rho_2 + \tilde{c}_{in}) > \dot{\Psi}(\rho_1 + \tilde{c}_{in})$ . Hence  $(\dot{\Psi}(\rho_2 + \tilde{c}_{in}) - \dot{\Psi}(\rho_1 + \tilde{c}_{in}))(\rho_2 - \rho_1) > 0$ . Hence

$$\langle A\rho_1 - A\rho_2, \rho_1 - \rho_2 \rangle > \frac{1}{\delta t} \|\rho_1 - \rho_2\|_0^2 + D \|\nabla(\rho_1 - \rho_2)\|_0^2.$$

Finally (ii) can be proved by taking  $\rho_1 = 0$  in (i). Q.E.D.

By Theorem 2.4.1 and Lemmas 2.4.3, 2.4.4, we have

**Corollary 2.4.2** There exists a unique solution to Problem  $(\tilde{P}_c^m)$  and hence also to  $(P_c^m)$  defined by (2.35).

## 2.5 Stability of the time-discretized Problem $P_c^m$

**Proposition 2.5.1** Let  $\tilde{c}^{m+1}$  be the solution of (2.40) for each integer  $m \in (0, N-1)$  with given  $\tilde{c}^j \in H^1(\Omega)$ ,  $\tilde{c}^j(x) \in [-1, 1]$  for  $j = 0, \dots, m$ ,  $\tilde{c}_{in} \in H^1(\Omega)$ ,  $\tilde{c}_{in}(x) \in [0, 1]$ , and  $\mathbf{u}^{m+1} \in H^1(\Omega)^d$  satisfying (U1), (U2). We have

$$\begin{aligned} \|\tilde{c}^{m+1}\|_0^2 + \|\tilde{c}^{m+1} - \tilde{c}^m\|_0^2 + D\delta t \|\nabla \tilde{c}^{m+1}\|_0^2 + \delta t \int_{\Gamma_{out}} (\mathbf{u}^{m+1} \cdot \mathbf{n})(\tilde{c}^{m+1})^2 \\ \leq \|\tilde{c}^m\|_0^2 + C_1 \delta t + C_2 \delta t \|\mathbf{u}^{m+1}\|_1^2 + C_3 \delta t \|\nabla \tilde{c}_{in}\|_0^2 \end{aligned} \quad (2.45)$$

*Proof.* By (2.40) with  $w = \tilde{c}^{m+1}$  we have

$$\begin{aligned} & \frac{1}{2\delta t} \|\tilde{c}^{m+1}\|_0^2 + \frac{1}{2\delta t} \|\tilde{c}^{m+1} - \tilde{c}^m\|_0^2 + D \|\nabla \tilde{c}^{m+1}\|_0^2 + \frac{1}{2} \int_{\Gamma_{out}} (\mathbf{u}^{m+1} \cdot \mathbf{n}) (\tilde{c}^{m+1})^2 \\ &= - \int_S i_0 \dot{\Psi}(c^{m+1}) \tilde{c}^{m+1} - \int_S \frac{\alpha i_0^3}{D} \sum_{j=0}^m c^j \delta t c^{m+1} \tilde{c}^{m+1} - \frac{1}{2} \int_{\Gamma_{out}} (\mathbf{u}^{m+1} \cdot \mathbf{n}) \tilde{c}_{in} \tilde{c}^{m+1} \\ & - \frac{1}{2} \int_{\Omega} (\mathbf{u}^{m+1} \cdot \nabla \tilde{c}^{m+1}) \tilde{c}_{in} dx + \frac{1}{2} \int_{\Omega} (\mathbf{u}^{m+1} \cdot \nabla \tilde{c}_{in}) \tilde{c}^{m+1} dx + \frac{1}{2\delta t} \|\tilde{c}^m\|_0^2 \end{aligned} \quad (2.46)$$

We estimate each term of the right hand side

$$\begin{aligned} & - \int_S i_0 \dot{\Psi}(c^{m+1}) \tilde{c}^{m+1} \leq i_0 \int_S |\dot{\Psi}(c^{m+1}) \tilde{c}^{m+1}| \leq i_0 |S|. \\ & - \int_S \frac{\alpha i_0^3}{D} \left( \sum_{j=0}^m c^j \delta t \right) c^{m+1} \tilde{c}^{m+1} \leq \frac{\alpha i_0^3}{D} \int_S \left( \sum_{j=0}^m c^j \delta t \right) c^{m+1} |\tilde{c}^{m+1}| \leq \frac{\alpha i_0^3}{D} \int_S m \delta t \leq \frac{\alpha i_0^3 T}{D} |S|. \\ & - \int_{\Gamma_{out}} (\mathbf{u}^{m+1} \cdot \mathbf{n}) \tilde{c}_{in} \tilde{c}^{m+1} \leq |\Gamma_{out}|^{\frac{1}{2}} \left( \int_{\Gamma_{out}} |\mathbf{u}^{m+1}|^2 \right)^{\frac{1}{2}} \leq C \|\mathbf{u}^{m+1}\|_1^2. \\ & - \int_{\Omega} (\mathbf{u}^{m+1} \cdot \nabla \tilde{c}^{m+1}) \tilde{c}_{in} dx \leq \int_{\Omega} |\mathbf{u}^{m+1} \cdot \nabla \tilde{c}^{m+1}| dx \leq \frac{1}{2D} \|\mathbf{u}^{m+1}\|_0^2 + \frac{D}{2} \|\nabla \tilde{c}^{m+1}\|_0^2. \\ & \int_{\Omega} (\mathbf{u}^{m+1} \cdot \nabla \tilde{c}_{in}) \tilde{c}^{m+1} dx \leq \int_{\Omega} |\mathbf{u}^{m+1} \cdot \nabla \tilde{c}_{in}| dx \leq \frac{1}{2D} \|\mathbf{u}^{m+1}\|_0^2 + \frac{D}{2} \|\nabla \tilde{c}_{in}\|_0^2. \end{aligned}$$

Collecting all terms leads to

$$\begin{aligned} & \frac{1}{2\delta t} \|\tilde{c}^{m+1}\|_0^2 + \frac{1}{2\delta t} \|\tilde{c}^{m+1} - \tilde{c}^m\|_0^2 + \frac{D}{2} \|\nabla \tilde{c}^{m+1}\|_0^2 + \frac{1}{2} \int_{\Gamma_{out}} (\mathbf{u}^{m+1} \cdot \mathbf{n}) (\tilde{c}^{m+1})^2 \\ & \leq \frac{1}{2\delta t} \|\tilde{c}^m\|_0^2 + C_1 + C_2 \|\mathbf{u}^{m+1}\|_1^2 + C_3 \|\nabla \tilde{c}_{in}\|_0^2 \end{aligned} \quad (2.47)$$

Multiplying both sides by  $2\delta t$  completes the proof. Q.E.D.

Summing (2.45) from 0 to  $m$ , leads to the following:

**Corollary 2.5.1** Let  $\mathbf{u}^{j+1} \in H^1(\Omega)^d$  be given satisfying (U1), (U2) for all  $j = 0, \dots, N-1$ . If  $\tilde{c}^0 \in H^1(\Omega)$ ,  $\tilde{c}^0(x) \in [-1, 1]$ ,  $\tilde{c}_{in} \in H^1(\Omega)$ ,  $\tilde{c}_{in}(x) \in [0, 1]$ , then (2.40) implies that

$$\begin{aligned} & \|\tilde{c}^{m+1}\|_0^2 + \sum_{j=0}^m \|\tilde{c}^{j+1} - \tilde{c}^j\|_0^2 + D \delta t \sum_{j=0}^m \|\nabla \tilde{c}^{j+1}\|_0^2 + \sum_{j=0}^m \delta t \int_{\Gamma_{out}} (\mathbf{u}^{j+1} \cdot \mathbf{n}) (\tilde{c}^{j+1})^2 \\ & \leq \|\tilde{c}^0\|_0^2 + C_1 T + C_2 \delta t \sum_{j=0}^m \|\mathbf{u}^{j+1}\|_1^2 + C_3 T \|\nabla \tilde{c}_{in}\|_0^2. \end{aligned} \quad (2.48)$$

**Proposition 2.5.2** Let  $\mathbf{u}^{j+1} \in H^1(\Omega)^d$  be given satisfying (U1), (U2) for all  $j = 0, \dots, N-1$ . If  $\tilde{c}^0 \in H^1(\Omega)$ ,  $\tilde{c}^0(x) \in [-1, 1]$ ,  $\tilde{c}_{in} \in H^1(\Omega)$ ,  $\tilde{c}_{in}(x) \in [0, 1]$ , then (2.40) implies that

$$\delta t \sum_{j=1}^m \left\| \frac{\tilde{c}^{j+1} - \tilde{c}^j}{\delta t} \right\|_{W'}^2 \text{ is uniformly bounded.} \quad (2.49)$$

*Proof.* By definition

$$\left\| \frac{\tilde{c}^{m+1} - \tilde{c}^m}{\delta t} \right\|_{W'} = \sup_{w_0 \in W} \frac{1}{\|w_0\|_1} \left\langle \frac{\tilde{c}^{m+1} - \tilde{c}^m}{\delta t}, w_0 \right\rangle. \quad (2.50)$$

By (2.40), with  $w = \frac{w_0}{\|w_0\|_1} \in W$ ,

$$\begin{aligned} \left\| \frac{\tilde{c}^{m+1} - \tilde{c}^m}{\delta t} \right\|_{W'} &= \sup_{w \in W, \|w\|=1} \left\{ - \int_{\Omega} D \nabla \tilde{c}^{m+1} \cdot \nabla w dx \right. \\ &\quad - \frac{1}{2} \int_{\Omega} [(\mathbf{u}^{m+1} \cdot \nabla \tilde{c}^{m+1})w - (\mathbf{u}^{m+1} \cdot \nabla w) \tilde{c}^{m+1}] dx - i_0 \int_S \dot{\Psi}(c^{m+1})w \\ &\quad - \int_S \frac{\alpha i_0^3}{D} \left( \sum_{j=0}^m c^j \delta t \right) c^{m+1} w - \frac{1}{2} \int_{\Gamma_{out}} (\mathbf{u}^{m+1} \cdot \mathbf{n}) c^{m+1} w \\ &\quad \left. - \frac{1}{2} \int_{\Omega} [(\mathbf{u}^{m+1} \cdot \nabla \tilde{c}_{in})w - (\mathbf{u}^{m+1} \cdot \nabla w) \tilde{c}_{in}] dx \right\}. \end{aligned} \quad (2.51)$$

We estimate all terms on the right hand side of (2.51)

$$-D \int_{\Omega} \nabla \tilde{c}^{m+1} \cdot \nabla w dx \leq D \|\nabla \tilde{c}^{m+1}\|_0 \|\nabla w\|_0 \leq D \|\tilde{c}^{m+1}\|_1 \|w\|_1 = D \|\tilde{c}^{m+1}\|_1, \quad (2.52)$$

$$\int_{\Omega} (\mathbf{u}^{m+1} \cdot \nabla w) \tilde{c}^{m+1} dx \leq \int_{\Omega} |\mathbf{u}^{m+1} \cdot \nabla w| \leq \|\mathbf{u}^{m+1}\|_0, \quad (2.53)$$

$$\begin{aligned} - \int_{\Omega} (\mathbf{u}^{m+1} \cdot \nabla \tilde{c}^{m+1}) w dx &= \int_{\Omega} (\mathbf{u}^{m+1} \cdot \nabla w) \tilde{c}^{m+1} dx - \int_{\partial\Omega} (\mathbf{u}^{m+1} \cdot \mathbf{n}) \tilde{c}^{m+1} w \\ &\leq \|\mathbf{u}^{m+1}\|_0 + \|\mathbf{u}^{m+1}\|_{\partial\Omega} \|w\|_{\partial\Omega} \leq C \|\mathbf{u}^{m+1}\|_1, \end{aligned} \quad (2.54)$$

$$- \int_S \dot{\Psi}(c^{m+1}) w \leq C |S|^{\frac{1}{2}} \|w\|_1 = C |S|^{\frac{1}{2}}, \quad (2.55)$$

$$- \int_S \left( \sum_{j=0}^m c^j \delta t \right) c^{m+1} w \leq \int_S T |w| \leq CT |S|^{\frac{1}{2}} \|w\|_1 = CT |S|^{\frac{1}{2}}, \quad (2.56)$$

$$- \int_{\Gamma_{out}} (\mathbf{u}^{m+1} \cdot \mathbf{n}) c^{m+1} w \leq \|\mathbf{u}^{m+1}\|_{\Gamma_{out}} \|w\|_{\Gamma_{out}} \leq C \|\mathbf{u}^{m+1}\|_1 \|w\|_1 = C \|\mathbf{u}^{m+1}\|_1, \quad (2.57)$$

$$\int_{\Omega} (\mathbf{u}^{m+1} \cdot \nabla w) \tilde{c}_{in} dx \leq \int_{\Omega} |\mathbf{u}^{m+1} \cdot \nabla w| \leq \|\mathbf{u}^{m+1}\|_0 \|w\|_1 = \|\mathbf{u}^{m+1}\|_0, \quad (2.58)$$

$$- \int_{\Omega} (\mathbf{u}^{m+1} \cdot \nabla \tilde{c}_{in}) w dx \leq C \|\mathbf{u}^{m+1}\|_1 \quad (\text{see (2.54)}). \quad (2.59)$$

Collecting (2.52)-(2.59) with (2.51), all multiplied by  $\delta t$ , gives

$$\delta t \left\| \frac{\tilde{c}^{m+1} - \tilde{c}^m}{\delta t} \right\|_{W'}^2 \leq C \delta t (1 + \|\tilde{c}^{m+1}\|_1^2 + \|\mathbf{u}^{m+1}\|_1^2). \quad (2.60)$$

By summing (2.60) from 0 to  $N-1$  and the boundedness given by Corollary 2.4.1 and Corollary



2.5.1, the proof is completed. Q.E.D.

## 2.6 Passage to the limit $\delta t \rightarrow 0$

Let us define

$$c_\delta : [0, T] \rightarrow H^1(\Omega), \quad c_\delta(t) = c^j \quad \text{if } t \in ((j-1)\delta t, j\delta t], \quad (2.61)$$

$$c_h : [0, T] \rightarrow H^1(\Omega), \quad c_h(t) = \frac{t - (j-1)\delta t}{\delta t} c^j + \frac{j\delta t - t}{\delta t} c^{j-1} \quad \text{if } t \in ((j-1)\delta t, j\delta t], \quad (2.62)$$

$$c_{\delta-} : [0, T] \rightarrow H^1(\Omega), \quad c_{\delta-}(t) = c^{j-1} \quad \text{if } t \in [(j-1)\delta t, j\delta t), \quad (2.63)$$

$$C_{\delta-} : [0, T] \rightarrow H^1(\Omega), \quad C_{\delta-}(t) = \sum_{k=1}^j c^{k-1} \delta t \quad \text{if } t \in [(j-1)\delta t, j\delta t), \quad (2.64)$$

for  $j = 1, \dots, N$ . Note that  $c_\delta$ ,  $c_h$ , and  $c_{\delta-}$  are in  $L^2(0, T; H^1(\Omega))$  and  $L^\infty(\Omega \times (0, T))$ . With these notations, problem  $(P_c^m)$  reads

$$\begin{aligned} & (\partial_t c_h, w) + \frac{1}{2} [(\mathbf{u}_\delta \cdot \nabla c_\delta, w) - (\mathbf{u}_\delta \cdot \nabla w, c_\delta)] \\ & + D(\nabla c_\delta, \nabla w) + \int_S i_0 \dot{\Psi}(c_\delta) w + \int_S \frac{\alpha i_0^3}{D} c_\delta C_{\delta-} w + \frac{1}{2} \int_{\Gamma_{out}} (\mathbf{u}_\delta \cdot \mathbf{n}) c_\delta w = 0. \end{aligned} \quad (2.65)$$

**Lemma 2.6.1**  $C_{\delta-}$  is in  $L^2(0, T; H^1(\Omega))$ .

*Proof.*

$$\begin{aligned} & \int_T \int_\Omega |\partial_{x_i} C_{\delta-}(t)|^2 dx dt \leq \int_0^T \int_\Omega \left( \delta t \sum_{k=1}^N |\partial_{x_i} c^{k-1}| \right)^2 dx dt \\ & = \int_0^T \int_\Omega \delta t^2 \left( \sum_{k=1}^N |\partial_{x_i} c^{k-1}| \right)^2 dx dt \leq \int_0^T \delta t^2 \cdot \frac{T}{\delta t} \sum_{k=1}^N |\partial_{x_i} c^{k-1}|^2 dx \\ & = T^2 \delta t \sum_{k=1}^N \int_\Omega |\partial_{x_i} c^{k-1}|^2 dx \leq C \end{aligned}$$

The last inequality is due to Corollary 2.5.1.

**Lemma 2.6.2**

$$\|c_\delta - c_h\|_{L^2((0, T) \times \Omega)} \leq \sqrt{\frac{\delta t}{3}} \left( \sum_{j=1}^N \|c^{j+1} - c^j\|_0^2 \right)^{\frac{1}{2}} \quad (2.66)$$

*Proof.*

$$\begin{aligned} c_\delta(t) - c_h(t) &= \frac{t - j\delta t}{\delta t} (c^j - c^{j-1}) \quad \text{for } (j-1)\delta t < t \leq j\delta t, \\ \int_{(j-1)\delta t}^{j\delta t} \|c_\delta(t) - c_h(t)\|_0^2 dt &= \frac{\delta t}{3} \|c^j - c^{j-1}\|_0^2. \end{aligned}$$

The proof can be completed by taking summation from  $j = 1$  to  $N$ .

**Corollary 2.6.1**

$$c_\delta - c_h \rightarrow 0 \quad \text{in } L^2((0, T) \times \Omega) \quad \text{as } \delta t \rightarrow 0. \quad (2.67)$$

By the boundedness given by Proposition 2.4.2, 2.5.2, and Corollary 2.5.1, there are subsequences of  $c_\delta$  and  $c_h$  (still denoted by  $c_\delta$  and  $c_h$ ), respectively such that

$$c_\delta \rightarrow c \quad \text{in } L^2(0, T; H^1(\Omega)) \text{ weakly,} \quad (2.68)$$

$$c_h \rightarrow c_* \quad \text{in } L^2(0, T; H^1(\Omega)) \text{ weakly,} \quad (2.69)$$

$$c_h \rightarrow c_* \quad \text{in } L^\infty(\Omega \times (0, T)) \text{ weak star,} \quad (2.70)$$

$$\partial_t c_h \rightarrow g \quad \text{in } L^2(0, T; W') \text{ weakly.} \quad (2.71)$$

By Corollary 2.6.1, we have  $c = c_*$ .

By a classical argument, see for instance [113], we have

$$g = \partial_t c. \quad (2.72)$$

Let

$$Y = \left\{ w \in L^2(0, T; H^1(\Omega)), \partial_t w \in L^2(0, T; W') \right\}.$$

By the Aubin-Lions Lemma,  $Y$  is compactly embedded in  $L^2(0, T; L^q(\Omega))$  with  $q < 6$  when  $d = 3$  and  $q < \infty$  when  $d = 2$ . Therefore, we have in particular

$$c_h \rightarrow c \quad \text{in } L^2((0, T) \times \Omega) \text{ strongly.} \quad (2.73)$$

Using Corollary 2.6.1 again, we get

$$c_\delta \rightarrow c \quad \text{in } L^2((0, T) \times \Omega) \text{ strongly.} \quad (2.74)$$

To see the convergence of the boundary term, we need the following lemma:

**Lemma 2.6.3** Let  $X$  be a normed linear space,  $D$  a dense subset of  $X'$ ,  $x_n$ ,  $n = 1, 2, \dots$  a uniform bounded sequence in  $X$ . If  $g(x_n) \rightarrow g(x)$  for all  $g \in D$ , then  $x_n \rightarrow x$  weakly in  $X$ .

The above Lemma can be found in Theorem 10.1 of [72].

**Lemma 2.6.4** Given  $c_\delta$  defined by (2.61), there exists a subsequence (still denoted by  $c_\delta$ ) satisfying (2.68) and the followings:

$$\dot{\Psi}(c_\delta) \rightarrow \dot{\Psi}(c) \quad \text{in } L^2(0, T; H^{\frac{1}{2}}(S)) \text{ weakly,} \quad (2.75)$$

$$c_\delta \int_0^t c_\delta(s) ds \rightarrow c \int_0^t c(s) ds \quad \text{in } L^2(0, T; H^{\frac{1}{2}}(S)) \text{ weakly.} \quad (2.76)$$

*Proof.* Let us prove that  $\dot{\Psi}(c_\delta)$  tends to  $\dot{\Psi}(c)$  weakly in  $L^2(0, T; H^1(\Omega))$ . First, we know that  $\dot{\Psi}(c_\delta)$  is bounded in  $\Omega \times [0, T]$  and we have  $\dot{\Psi}(c_\delta) = c_\delta - \frac{\alpha c_\delta^2}{2}$  a.e. since  $c_\delta \leq 1$  a.e.. Moreover, since  $\alpha < 1$ , we have

$$\begin{aligned} \int_0^T \int_\Omega |\partial_{x_i} \dot{\Psi}(c_\delta)|^2 dx dt &= \int_0^T \int_\Omega |\partial_{x_i} c_\delta - \alpha c_\delta \partial_{x_i} c_\delta|^2 dx dt \\ &= \int_0^T \int_\Omega |(1 - \alpha c_\delta) \partial_{x_i} c_\delta|^2 dx dt = \int_0^T \int_\Omega |1 - \alpha c_\delta|^2 |\partial_{x_i} c_\delta|^2 dx dt \\ &\leq \int_0^T \int_\Omega |\partial_{x_i} c_\delta|^2 dx dt < \infty. \end{aligned}$$

Therefore,  $\dot{\Psi}$  converges weakly in  $L^2(0, T; H^1(\Omega))$ . To identify its limit, let  $w \in C([0, T] \times \bar{\Omega})$ . Then (2.74) implies that

$$\int_0^T \int_{\Omega} \dot{\Psi}(c_{\delta}) w dx dt \rightarrow \int_0^T \int_{\Omega} \dot{\Psi}(c) w dx dt$$

and (2.74) and (2.68) imply that

$$\int_0^T \int_{\Omega} \partial_{x_i} \dot{\Psi}(c_{\delta}) w dx dt \rightarrow \int_0^T \int_{\Omega} \partial_{x_i} \dot{\Psi}(c) w dx dt.$$

This gives the desired convergence. By the continuity of the trace mapping

$$\phi \mapsto \phi|_{\partial\Omega}$$

for the weak topology, we deduce that

$$\dot{\Psi}(c_{\delta}) \rightarrow \dot{\Psi}(c) \text{ weakly in } L^2(0, T; H^{\frac{1}{2}}(S)). \quad (2.77)$$

For (2.76), we define  $r(t, c_{\delta}) := c_{\delta} \int_0^t c_{\delta}(s) ds$  in  $(0, T) \times \Omega$ . To begin with, we observe that  $\int_0^t c_{\delta}(s) ds \rightarrow \int_0^t c(s) ds$  strongly in  $L^2((0, T) \times \Omega)$ . This can be checked by the estimate:

$$\begin{aligned} \int_0^T \int_{\Omega} \left| \int_0^t (c_{\delta}(s) - c(s)) ds \right|^2 dx dt &\leq \int_0^T \int_{\Omega} t \int_0^t |c_{\delta}(s) - c(s)|^2 ds dx dt \\ &\leq \int_0^T t \int_0^T \int_{\Omega} |c_{\delta}(s) - c(s)|^2 dx ds dt = \frac{1}{2} T^2 \int_0^T \int_{\Omega} |c_{\delta}(s) - c(s)|^2 dx ds \\ &\rightarrow 0 \text{ as } \delta t \rightarrow 0. \end{aligned}$$

Let  $w \in C([0, T] \times \bar{\Omega})$ . Since  $c_{\delta}$  strongly converges to  $c$  in  $L^2((0, T) \times \Omega)$ , we have

$$\int_0^T \int_{\Omega} r(t, c_{\delta}) w dx dt \rightarrow \int_0^T \int_{\Omega} r(t, c) w dx dt. \quad (2.78)$$

We differentiate  $r(t, c_{\delta})$ :

$$\partial_{x_i} r(t, c_{\delta}) = \partial_{x_i} c_{\delta} \int_0^t c_{\delta}(s) ds + c_{\delta} \int_0^t \partial_{x_i} c_{\delta}(s) ds. \quad (2.79)$$

We have the boundedness for the first term on the right hand side:

$$\begin{aligned} \int_0^T \int_{\Omega} |\partial_{x_i} c_{\delta}|^2 \left| \int_0^t c_{\delta}(s) ds \right|^2 dx dt &\leq \int_0^T \int_{\Omega} t |\partial_{x_i} c_{\delta}|^2 dx dt \\ &\leq T \int_0^T \int_{\Omega} |\partial_{x_i} c_{\delta}|^2 dx dt < \infty \end{aligned} \quad (2.80)$$

Using the fact that both  $\partial_{x_i} c_{\delta} \rightarrow \partial_{x_i} c$  weakly in  $L^2((0, T) \times \Omega)$  and  $\int_0^t c_{\delta}(s) ds \rightarrow \int_0^t c(s) ds$

strongly in  $L^2((0, T) \times \Omega)$ , we have

$$\int_0^T \int_{\Omega} \partial_{x_i} c_{\delta} \left( \int_0^t c_{\delta}(s) ds \right) w dx dt \rightarrow \int_0^T \int_{\Omega} \partial_{x_i} c \left( \int_0^t c(s) ds \right) w dx dt. \quad (2.81)$$

The second term is bounded as well:

$$\begin{aligned} & \int_0^T \int_{\Omega} \left| \int_0^t \partial_{x_i} c_{\delta}(s) ds \right|^2 dx dt \leq \int_0^T \int_{\Omega} t \int_0^t |\partial_{x_i} c_{\delta}(s)|^2 ds dx dt \\ &= \int_0^T t \int_0^t \int_{\Omega} |\partial_{x_i} c_{\delta}(s)|^2 dx ds dt \leq \int_0^T t \int_0^T \int_{\Omega} |\partial_{x_i} c_{\delta}(s)|^2 dx ds dt \\ &= \frac{1}{2} T^2 \int_0^T \int_{\Omega} |\partial_{x_i} c_{\delta}(s)|^2 dx dt < \infty \end{aligned} \quad (2.82)$$

And we observe that

$$\begin{aligned} & \int_0^T \int_{\Omega} \left( \int_0^t \partial_{x_i} c_{\delta}(s) ds \right) w dx dt \\ &= \int_0^T \int_0^t \left( \int_{\Omega} \partial_{x_i} c_{\delta}(s) w dx \right) ds dt \rightarrow \int_0^T \left( \int_0^t \int_{\Omega} \partial_{x_i} c(s) w dx ds \right) dt \end{aligned}$$

because  $w(t)$  for fixed  $t$  is continuous in  $\Omega$ . Now, we have  $c_{\delta} \rightarrow c$  in  $L^2((0, T) \times \Omega)$  strongly and  $\int_0^t \partial_{x_i} c_{\delta}(s) ds \rightarrow \int_0^t \partial_{x_i} c(s) ds$  weakly in  $L^2((0, T) \times \Omega)$ . This implies that

$$\int_0^T \int_{\Omega} c_{\delta} \left( \int_0^t \partial_{x_i} c_{\delta}(s) ds \right) w(t) dx dt \rightarrow \int_0^T \int_{\Omega} c \left( \int_0^t \partial_{x_i} c(s) ds \right) w dx dt$$

By (2.82) and Lemma A.3.3 below, we have  $c_{\delta} \int_0^t \partial_{x_i} c_{\delta}(s) ds \rightarrow c \int_0^t \partial_{x_i} c(s) ds$  weakly in  $L^2((0, T) \times \Omega)$ .

Collecting all the weak convergence results above, we conclude that  $r(t, c_{\delta}) \rightarrow r(t, c)$  in  $L^2(0, T; H^1(\Omega))$  weakly. By the continuity of the trace for the weak topology, we have  $r(t, c_{\delta}) \rightarrow r(t, c)$  in  $L^2(0, T; H^{\frac{1}{2}}(S))$  weakly. Q.E.D.

**Lemma 2.6.5**  $C_{\delta-}$  defined in (2.64) satisfies

$$\left\| C_{\delta-} - \int_0^t c_{\delta}(s) ds \right\|_{L^2(0, T; H^1(\Omega))} \leq C \delta t \quad (2.83)$$

*Proof.* For all  $t \in [(j-1)\delta t, j\delta t)$ ,

$$\begin{aligned} C_{\delta-}(t) - \int_0^t c_{\delta}(s) ds &= \sum_{k=1}^j c^{k-1} \delta t - \sum_{k=1}^{j-1} c^k \delta t - c^j (t - (j-1)\delta t) \\ &= c^0 \delta t - c^j (t - (j-1)\delta t). \end{aligned}$$

But for  $t \in [(j-1)\delta t, j\delta t]$ , we have  $0 \leq t - (j-1)\delta t \leq \delta t$ . Therefore

$$\left| C_{\delta-}(t) - \int_0^t c_{\delta}(s)ds \right| \leq \delta t |c^0 + c^j|.$$

On the other hand,

$$\begin{aligned} \partial_{x_i} C_{\delta-}(t) - \partial_{x_i} \int_0^t c_{\delta}(s)ds &= \partial_{x_i} C_{\delta-}(t) - \int_0^t \partial_{x_i} c_{\delta}(s)ds \\ &= \partial_{x_i} c^0 \delta t - \partial_{x_i} c^j (t - (j-1)\delta t). \end{aligned}$$

Hence, we have

$$\left| \partial_{x_i} \left( C_{\delta-}(t) - \int_0^t c_{\delta}(s)ds \right) \right| \leq \delta t |\partial_{x_i} (c^0 + c^j)|.$$

Therefore,

$$\begin{aligned} \left\| C_{\delta-} - \int_0^t c_{\delta}(s)ds \right\|_{L^2(0,T;H^1(\Omega))}^2 &= \int_0^T \left\| C_{\delta t-}(t) - \int_0^t c_{\delta}(s)ds \right\|_1^2 \\ &\leq \sum_{j=1}^N \int_{(j-1)\delta t}^{j\delta t} (\delta t)^2 \|c^0 + c^j\|_1^2 \\ &\leq 2 \sum_{j=1}^N \int_{(j-1)\delta t}^{j\delta t} (\delta t)^2 (\|c^0\|_1^2 + \|c^j\|_1^2) \\ &\leq 2\|c^0\|_1^2 (\delta t)^2 + 2(\delta t)^2 \sum_{j=1}^N \delta t \|c^j\|_1^2 \\ &\leq C(\delta t)^2 \end{aligned}$$

Q.E.D.

**Proof of Theorem 2.3.1.**

Now, we are in a position to pass to the limit in (2.65). Take any  $w = v(x)\lambda(t)$ , where  $v \in W \cap W^{1,\infty}(\Omega)$  and  $\lambda \in W_0^{1,\infty}(0, T)$ . Then

$$\begin{aligned} & - \int_0^T (c_h, v) \lambda'(t) dt + \frac{1}{2} \int_0^T [(\mathbf{u}_{\delta} \cdot \nabla c_{\delta}, v) - (\mathbf{u}_{\delta} \cdot \nabla v, c_{\delta})] \lambda dt \\ & + \int_0^T D(\nabla c_{\delta}, \nabla v) \lambda dt + \int_0^T \int_S i_0 \dot{\Psi}(c_{\delta}) v \lambda(t) dt + \int_0^T \int_S \frac{\alpha i_0^3}{D} c_{\delta} C_{\delta-} v \lambda(t) dt \\ & + \frac{1}{2} \int_0^T \int_{\Gamma_{out}} (\mathbf{u}_{\delta} \cdot \mathbf{n}) c_{\delta} v \lambda(t) dt = 0. \end{aligned}$$

Since  $\mathbf{u}_{\delta} \rightarrow \mathbf{u}$  strongly in  $L^2(\Omega \times (0, T))$  and  $\nabla c_{\delta} \rightarrow \nabla c$  weakly in  $L^2(\Omega \times (0, T))$ , the regularity of  $v$  and  $\lambda$  implies that

$$- \int_0^T (c_h, v) \lambda'(t) dt \rightarrow - \int_0^T (c, v) \lambda'(t) dt = \int_0^T \langle \partial_t c, v \rangle_{W', W} \lambda dt, \quad (2.84)$$

$$\frac{1}{2} \int_0^T [(\mathbf{u}_{\delta} \cdot \nabla c_{\delta}, v) - (\mathbf{u}_{\delta} \cdot \nabla v, c_{\delta})] \lambda dt \rightarrow \frac{1}{2} \int_0^T [(\mathbf{u} \cdot \nabla c, v) - (\mathbf{u} \cdot \nabla v, c)] \lambda dt, \quad (2.85)$$

$$\int_0^T D(\nabla c_\delta, \nabla c) \lambda dt \rightarrow \int_0^T D(\nabla c, \nabla v) \lambda dt. \quad (2.86)$$

Similarly, the weak convergence of  $\dot{\Psi}(c_\delta)$  to  $\dot{\Psi}(c)$  in  $L^2(0, T; H^{\frac{1}{2}}(S))$  implies that

$$\int_0^T \int_S i_0 \dot{\Psi}(c_\delta) v \lambda(t) dt \rightarrow \int_0^T \int_S \dot{\Psi}(c) v \lambda(t) dt, \quad (2.87)$$

and the weak convergence of  $c_\delta C_{\delta-}$  to  $c \int_0^t c$  in  $L^2(0, T; H^{\frac{1}{2}}(S))$  implies that

$$\int_0^T \int_S c_\delta C_{\delta-} v \lambda(t) dt \rightarrow \int_0^T \int_S c \left( \int_0^t c(s) ds \right) v \lambda(t) dt. \quad (2.88)$$

Finally, we consider the last term  $\frac{1}{2} \int_0^T \int_{\Gamma_{out}} (\mathbf{u}_\delta \cdot \mathbf{n}) c_\delta v \lambda(t)$ . Given the construction of  $\mathbf{u}_\delta$  in Section 2.4, we have:  $\mathbf{u}_\delta \rightarrow \mathbf{u}$  weakly in  $L^2(0, T; H^1(\Omega)^d)$  and  $\mathbf{u}_\delta \rightarrow \mathbf{u}$  strongly in  $L^2(0, T; L^4(\Omega)^d)$  (thanks to the strong convergence of  $\mathbf{u}_\delta$  by (2.32),  $H^1(\Omega)^d$  can be replaced by any space  $X$  so that  $H^1(\Omega) \subset\subset X$ . Here we take  $X = L^4(\Omega)^d$ , which is compatible with  $d = 3$ ; the exponent has to be less than 6). We use Green's formula:

$$\int_0^T \int_{\Gamma_{out}} (\mathbf{u}_\delta \cdot \mathbf{n}) c_\delta v \lambda = \int_0^T \int_\Omega \nabla \cdot (\mathbf{u}_\delta c_\delta) v \lambda + \int_0^T \int_\Omega (c_\delta \mathbf{u}_\delta \cdot \nabla v) \lambda \quad (2.89)$$

for all  $\lambda \in L^\infty(0, T)$  and for all smooth  $v$  that vanish on  $\partial\Omega \setminus \Gamma_{out}$ . It suffices to prove the convergence of each term to the desired limit.

1) For all  $v \in L^4(\Omega)$  and for all  $\lambda \in L^\infty(0, T)$ :

$$\begin{aligned} \int_0^T \int_\Omega \nabla \cdot (\mathbf{u}_\delta c_\delta) v \lambda &= \int_0^T \int_\Omega \mathbf{u}_\delta \cdot \nabla c_\delta v \lambda \\ &= \int_0^T \int_\Omega (\mathbf{u}_\delta - \mathbf{u}) \cdot \nabla c_\delta v \lambda + \int_0^T \int_\Omega \mathbf{u} \cdot \nabla c_\delta v \lambda \\ &\leq \|\mathbf{u}_\delta - \mathbf{u}\|_{L^2(0, T; L^4(\Omega))} \|\nabla c_\delta\|_{L^2(\Omega \times (0, T))} \|\lambda\|_{L^\infty(0, T)} \|v\|_{L^4(\Omega)} + \int_0^T \int_\Omega \mathbf{u} \cdot \nabla c_\delta v \lambda. \end{aligned}$$

It is noted that  $\mathbf{u} v \lambda \in L^2(0, T; L^2(\Omega)^d)$  and  $\nabla c_\delta \rightarrow \nabla c$  weakly in  $L^2(0, T; L^2(\Omega)^d)$ , we have

$$\int_0^T \int_\Omega \nabla \cdot (\mathbf{u}_\delta c_\delta) v \lambda \rightarrow \int_0^T \int_\Omega (\mathbf{u} \cdot \nabla c) v \lambda = \int_0^T \int_\Omega \nabla \cdot (\mathbf{u} c) v \lambda. \quad (2.90)$$

2) For all  $v \in H^1(\Omega)$ ,  $\lambda \in L^\infty(\Omega)$

$$\begin{aligned} \int_0^T \int_\Omega (c_\delta \mathbf{u}_\delta \cdot \nabla v) \lambda &= \int_0^T \int_\Omega c_\delta (\mathbf{u}_\delta - \mathbf{u}) \cdot \nabla v \lambda + \int_0^T \int_\Omega \mathbf{u} (c_\delta - c) \cdot \nabla v \lambda + \int_0^T \int_\Omega c (\mathbf{u} \cdot \nabla v) \lambda \\ &\leq \|\mathbf{u}_\delta - \mathbf{u}\|_{L^2(0, T; L^2(\Omega)^d)} \|c_\delta\|_{L^\infty(\Omega \times (0, T))} \|\nabla v\|_0 \|\lambda\|_{L^\infty(\Omega)} \\ &\quad + \|\mathbf{u}\|_{L^2(0, T; L^4(\Omega)^d)} \|c_\delta - c\|_{L^2(0, T; L^4(\Omega)^d)} \|\nabla v\|_0 \|\lambda\|_{L^\infty(\Omega)} + \int_0^T \int_\Omega c (\mathbf{u} \cdot \nabla v) \lambda. \end{aligned}$$

Therefore

$$\begin{aligned}
& \int_0^T \langle \partial_t c, v \rangle_{W', W} \lambda dt + \frac{1}{2} \int_0^T ((\mathbf{u} \cdot \nabla c, v) - (\mathbf{u} \cdot \nabla v, c)) \lambda dt \\
& + \int_0^T D(\nabla c, \nabla v) \lambda dt + \int_0^T \int_S i_0 \dot{\Psi}(c) v \lambda dt + \int_0^T \int_S \frac{\alpha i_0^3}{D} c \left( \int_0^t c(s) ds \right) v \lambda dt \\
& + \frac{1}{2} \int_0^T \int_{\Gamma_{out}} (\mathbf{u} \cdot \mathbf{n}) c v \lambda dt = 0
\end{aligned} \tag{2.91}$$

for all  $\lambda \in W_0^{1,\infty}(0, T)$  and for all  $v \in W^{1,\infty}(\Omega)$ . This gives the equations a.e. in  $(0, T)$ .

To recover the initial condition, we take  $\lambda \in W^{1,\infty}(0, T)$ ,  $\lambda(T) = 0$ ,  $\lambda(0) \neq 0$ , and  $v \in W^{1,\infty}(\Omega)$ . We consider (2.65) such that all terms are identical except the first:

$$\int_0^T (\partial_t c_h, v) \lambda dt = \int_0^T \partial_t (c_h, v) \lambda dt = - \int_0^T (c_h, v) \lambda'(t) - (c^0, v) \lambda(0). \tag{2.92}$$

When passing to the limit, we obtain

$$\begin{aligned}
& \int_0^T \langle \partial_t c, v \rangle_{W', W} \lambda dt = - \int_0^T (c, v) \lambda'(t) - (c^0, v) \lambda(0) \\
& = \int_0^T \frac{d}{dt} (c, v) \lambda + (c(0), v) \lambda(0) - (c^0, v) \lambda(0) \\
& = \int_0^T \langle \partial_t c, v \rangle_{W', W} \lambda dt + (c(0), v) \lambda(0) - (c^0, v) \lambda(0).
\end{aligned} \tag{2.93}$$

Therefore

$$(c(0), v) = (c^0, v), \quad \forall v \in W \cap W^{1,\infty}(\Omega).$$

This implies that  $c(0) = c^0$ .

The above shows that Problem  $(P_c)$  has a unique solution, which satisfies  $0 \leq c \leq 1$ ; it is also the solution of  $(P)$ . Q.E.D.

### 2.6.1 On the boundary condition (2.19) which contains $\partial_t c$

To prove existence a similar strategy is taken:  $\partial_t c$  is replaced by  $(c^{m+1} - c^m)/\delta t$ , existence is shown and then convergence when  $\delta t \rightarrow 0$ .

The proof of existence of the time-discretized problem is exactly the same but with  $\phi$  redefined as

$$\phi_m(c^{m+1}) = i_0 \dot{\Psi}(c^{m+1}) + \alpha i_0 \left( \frac{i_0^2}{D} - \frac{1}{\delta t} \right) \left( \sum_{j=0}^m c^j \delta t \right) c^{m+1}.$$

Convergence with  $\delta t \rightarrow 0$  requires more regularity, which can be obtained from the PDE differentiated in time.

## 2.7 Numerical simulations

The rectangular domain of size  $0.025 \text{ mm} \times 0.005 \text{ mm}$  is the initial physical domain. The electroprocess is simulated up to time  $T = 5000$ .

### 2.7.1 Scalings

The simulation will be done with dimensionless variables. Let  $L, C$  and  $U$  be representative length, concentration and velocity of the physical system. Then it is easy to see that the dimensionless equation for  $c$  is the same as the original equation but with  $\tilde{D}/(LU)$  instead of  $D$ , where  $\tilde{D}$  is the physical molecular diffusion. Similarly because (2.7) becomes

$$-D \frac{\partial c}{\partial n} = \frac{i_0}{U} c, \quad \mathbf{u} = -\alpha C \frac{i_0}{U} \mathbf{cn},$$

the original form holds but with  $i_0/U$  redefined as  $i_0$  and  $\alpha C$  redefined as  $\alpha$ .

It is well known that the dimensionalized Navier-Stokes equation has the inverse Reynolds number  $\tilde{\nu}/(UL)$  redefined as  $\nu$ , where  $\tilde{\nu}$  being the kinematic viscosity.

The parameters of nickel ion given in [66] are  $i_0 = \tilde{i}_0/(zF)$  with  $\tilde{i}_0 = 0.001 \text{ A} \cdot \text{mm}^{-2}$ , the number of electrons involves in the reaction  $z = 2$  and the Faraday constant  $F = 96487 \text{ s} \cdot \text{A} \cdot \text{mol}^{-1}$ ,  $C = 3 \times 10^{-7} \text{ mol} \cdot \text{mm}^{-3}$ .

For electrodeless plating we may take  $U = 1 \text{ mm} \cdot \text{s}^{-1}$ ,  $L = 0.005 \text{ mm}$ ,  $\tilde{D} = 1 \times 10^{-4} \text{ mm}^2 \cdot \text{s}^{-1}$ ,  $\alpha = 6590 \text{ mm}^3 \cdot \text{mol}^{-1}$ , and  $\tilde{\nu} = 1.2 \text{ mm}^2 \cdot \text{s}^{-1}$ .

So in the end the numerical tests are done on a rescaled domain  $\Omega = (0, 5) \times (0, 1)$  with

$$\alpha = 0.002085, \quad i_0 = 0.017273, \quad D = 0.02, \quad \nu = 240,$$

### 2.7.2 Numerical algorithm

The finite element method is used for spacial discretization. Let  $\mathcal{T}_h$  be a triangulation consisting of  $K$  triangles  $\{T_k\}_{k=1}^K$  with the standard conformity hypothesis. We define the finite element space which will be used in this section:

$$\begin{aligned} W_h &:= \{w \in C^0(\bar{\Omega}) : w|_{T_k} \in P^1 \ \forall T_k \in \mathcal{T}_h, \ w|_{\Gamma_{in}} = 0\}, \\ C_h &:= \{w \in C^0(\bar{\Omega}) : w|_{T_k} \in P^1, \ \forall T_k \in \mathcal{T}_h\}, \\ \mathbf{V}_h &:= \{\mathbf{v} \in C^0(\bar{\Omega})^2 : \mathbf{v}|_{T_k} \in (P^2)^2, \ \forall T_k \in \mathcal{T}_h\}, \\ \mathbf{J}_h &:= \{\mathbf{v} \in C^0(\bar{\Omega})^2 : \mathbf{v}|_{T_k} \in (P^2)^2 \ \forall T_k \in \mathcal{T}_h, \ \mathbf{v}|_{\partial\Omega \setminus \Gamma_{out}} = 0\}, \\ Q_h &:= C_h. \end{aligned} \tag{2.94}$$

#### Solving concentration profile $c_h^{m+1}$ with known velocity field $\mathbf{u}_h^{m+1}$

We use the  $P^1$  finite element method for Problem  $(P_c^m)$  to define  $\{c_h^m\}_{m \geq 0}$ . Given  $\mathbf{u}_h^{m+1} \in \mathbf{V}_h$ , one must solve the finite dimensional problem  $(P_h^m)$  defined to be  $(P_c^m)$  with  $W_h$  instead of  $W$  in (2.35): find  $c_h^{m+1} \in C_h$  satisfying, for all  $w_h \in W_h$ ,

$$\begin{aligned} &\int_{\Omega} \frac{c_h^{m+1} - c_h^m}{\delta t} w_h dx + \int_{\Omega} [(\mathbf{u}_h^{m+1} \cdot \nabla c_h^{m+1}) w_h \\ &+ D \int_{\Omega} \nabla c_h^{m+1} \cdot \nabla w_h dx + \int_S \left( 1 + \frac{\alpha i_0^2}{D} \left( \sum_{j=1}^m c_h^j \delta t \right) \right) i_0 c_h^{m+1} w_h = 0, \\ &c_h^{m+1}|_{\Gamma_{in}} = c_{in,h} \end{aligned} \tag{2.95}$$

In the above,  $c_{in,h}$  is the piecewise linear interpolate of  $c_{in}$ .



Since  $\mathbf{u}_h^{m+1}$  and  $\{c_h^j\}_{j \leq m}$  are given, (2.95) leads to a linear system by assigning  $w_h$  to be the P1 hat functions in a standard way. We apply UMFPACK[32] for solving the linear system at each time step.

### Solving velocity field $\mathbf{u}_h^{m+1}$ with known concentration profile $c_h^{m+1}$

For the Navier-Stokes equation we use the  $P^2/P^1$  triangular Taylor-Hood element [10] and we denote by  $\mathbf{u}_h^m, p_h^m$  the finite element solution and by  $\mathbf{V}_h, Q_h$  the corresponding finite element space. The variational formulation is: Find  $\mathbf{u}_h^{m+1} \in \mathbf{V}_h$  and  $p_h^{m+1} \in Q_h$  satisfying

$$\begin{aligned} & \int_{\Omega} \frac{\mathbf{u}_h^{m+1} - \mathbf{u}_h^m}{\delta t} \cdot \mathbf{v}_h dx + \int_{\Omega} [(\mathbf{u}_h^m \cdot \nabla) \mathbf{u}_h^{m+1}] \cdot \mathbf{v}_h dx + \nu \int_{\Omega} \nabla \mathbf{u}_h^{m+1} : \nabla \mathbf{v}_h dx \\ & - \int_{\Omega} (p_h^{m+1} \nabla \cdot \mathbf{v}_h + q_h \nabla \cdot \mathbf{u}_h^{m+1} + \epsilon p_h^{m+1} q_h) dx = 0, \\ & \mathbf{u}_h^{m+1} = \mathbf{u}_{in_h} \text{ on } \Gamma_{in}, \quad \mathbf{u}_h^{m+1} = 0 \text{ on } \Gamma_{wall}, \quad \mathbf{u}_h^{m+1} = -\alpha i_0 c_h^{m+1} \mathbf{n} \text{ on } S \end{aligned} \quad (2.96)$$

for all  $\mathbf{v}_h \in \mathbf{J}_h$  and  $q_h \in Q_h$ ;  $\epsilon$  is a small regularization parameter which is taken to be  $10^{-12}$  in our computer implementation. In the above,  $\mathbf{u}_{in_h}$  is the  $P^2$  interpolation of  $\mathbf{u}_{in}$ .

With known  $\mathbf{u}_h^m$  and  $c_h^{m+1}$ , (2.96) leads to a linear system for the degrees of freedom of  $\mathbf{u}_h^{m+1}$  and  $p_h^{m+1}$  which is solved with the numerical library UMFPACK[32], at each  $m$ .

**Remark 2.7.1** If mass-lumping is used and the triangulation has no obtuse angle, the positivity of (2.95) can be guaranteed by the same argument in the proof of Proposition 2.4.2. Therefore, the assumption (U1) holds for  $\mathbf{u}_h^{m+1}$ . Again, (U2) does not hold for the system (2.96) in general. In practical numerical implementation, the natural outflow boundary condition

$$-\nu \frac{\partial \mathbf{u}_h^{m+1}}{\partial n} + p_h^{m+1} \mathbf{n} = 0$$

does no harm to (U2) when the velocity field is closed to a Poiseuille flow (for instance, the numerical tests conducted in Sections 7.3 and 7.4).

### Iteration algorithm

The coupled system (2.95)-(2.96) is solved iteratively. We replace  $c_h^{m+1}$  by  $c^*$  in (2.95) and solve (2.96). We denote the solution by  $\mathbf{u}^*$ . Then we replace  $\mathbf{u}_h^{m+1}$  by  $\mathbf{u}^*$  in order to get the new  $c^*$ , until  $\|\mathbf{u}_{new}^* - \mathbf{u}_{old}^*\|_0 + \|c_{new}^* - c_{old}^*\|_0$  is sufficiently small.

To validate the method we need to compare with the original free boundary problem. It is solved with a similar iterative fixed point like process but the mesh needs to be rebuilt when the free boundary is updated. It is done by a scaling on  $y$ -coordinate at each time step  $t^j$ :  $y \mapsto (1 - \alpha i_0 c_h^j \delta t) y$ .

$\delta t$	$L^2$ error	$\delta t$	$H^1$ error	$\delta t$	$L^2$ error
0.16	$1.01723 \times 10^{-5}$	0.16	$1.03365 \times 10^{-5}$	0.16	$1.01722 \times 10^{-5}$
0.08	$4.74704 \times 10^{-6}$	0.08	$4.82368 \times 10^{-6}$	0.08	$4.74701 \times 10^{-6}$
0.04	$2.03444 \times 10^{-6}$	0.04	$2.06729 \times 10^{-6}$	0.04	$2.03443 \times 10^{-6}$
0.02	$6.78147 \times 10^{-7}$	0.02	$6.89107 \times 10^{-7}$	0.02	$6.78142 \times 10^{-7}$
		$\delta t$	$H^1$ error		
		0.16	$1.03365 \times 10^{-5}$		
		0.08	$4.82367 \times 10^{-6}$		
		0.04	$2.06729 \times 10^{-6}$		
		0.02	$6.89103 \times 10^{-7}$		

Table 2.1: Convergence when  $\delta t \rightarrow 0$ :  $L^2$  and  $H^1$  relative error at  $T = 100$  for the scheme with the nonlinear transpiration approximation and  $\nu = 240$  (left columns) and  $\nu = 0.01$  (right columns). A uniform triangular mesh  $150 \times 30$  is used.;  $c_{\delta t=0.01}$  is used as reference solution.

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<b>Data :</b> $\mathbf{u}_h^m, p_h^m, c_h^m$ , and $y$	
1	Set initial data $\mathbf{u}_0, c_0$ ;
2	<b>for</b> $m$ <b>do</b>
3	$c^* = c_h^m$ ;
4	<b>while</b> $\ \mathbf{u}_{new}^* - \mathbf{u}_{old}^*\ _0 + \ c_{new}^* - c_{old}^*\ _0 \geq \text{tolerance}$ <b>do</b>
5	Solve (2.95) to get $c_{new}^*$ ;
6	Solve (2.96) to get $\mathbf{u}_{new}^*$ and $p_{new}^*$ ;
7	<b>end</b>
8	$c_h^{m+1} = c_{new}^*$ ;
9	$\mathbf{u}_h^{m+1} = \mathbf{u}_{new}^*$ ;
10	For the free boundary case change the mesh by $y \leftarrow (1 - \alpha i_0 c_h^{m+1} \delta t)y$ ;
11	<b>end</b>

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### 2.7.3 Numerical results at low Reynolds number

The initial and inflow values are

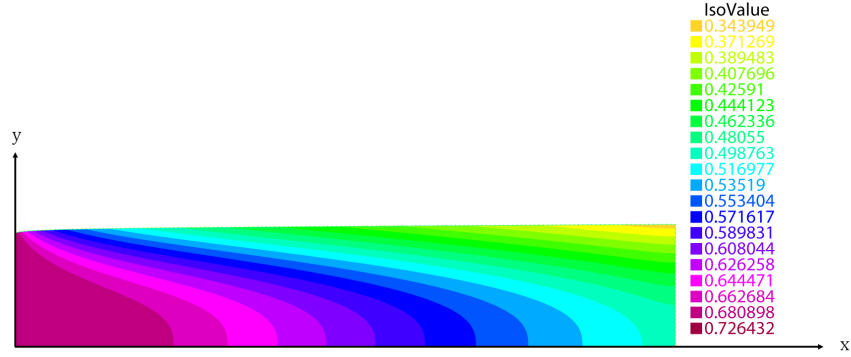
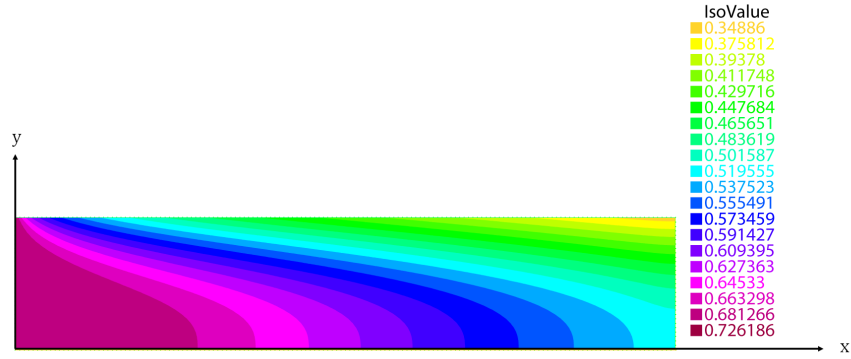
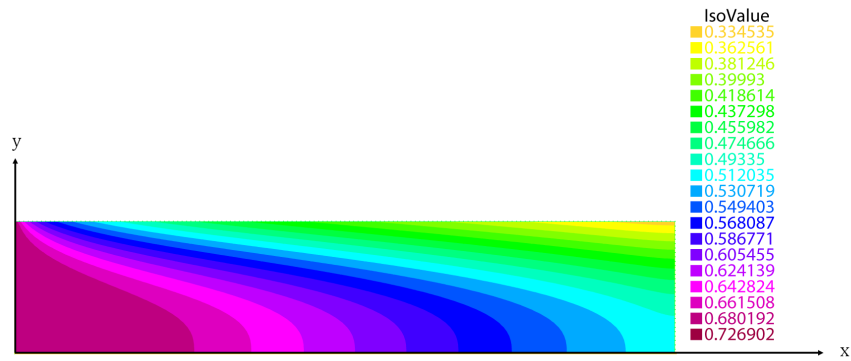
$$c_0 = \cos(\lambda y), \quad \mathbf{u}_0 = y(1 - y); \quad c_{in} = c_0|_{\Gamma_{in}} \exp(-D\lambda^2 t), \quad \mathbf{u}_{in} = \mathbf{u}_0|_{\Gamma_{in}}.$$

A uniform triangular mesh  $150 \times 30$  for the initial domain for each test so that the time-discrete error can be emphasized.

We compare the results obtained using a time dependent domain (Figure 2.3a) with the results using a fixed domain and the linear condition (2.7) (see Figure 2.3b) and finally with the nonlinear condition (2.12) (see Figure 2.3c).

On Figure 2.4 the free boundary and the reconstructed free boundaries are displayed using  $\eta$  given by (2.8).

The convergence with respect to time step size is shown on Table 2.1, computed at an intermediate time  $T = 100$ . Since no exact solution is available, the numerical solution with time step  $\delta t = 0.01$  is taken as the reference solution. The numerical results in Table 2.1 show a first order convergence in  $L^2$  error conformed with the estimates given in Appendix B (see Figure 2.5). The weak first order convergence of  $H^1$  error is also proved in Appendix B. However the numerical results show strong first order  $H^1$  convergence for this test problem (see Figure 2.6).

(a) Intensity map of  $c$  computed with a free boundary on a moving mesh.(b) Intensity map of  $c$  computed by the linear transpiration approximation.(c) Intensity map of  $c$  computed by nonlinear transpiration approximation.Figure 2.3: The solution profiles of numerical experiments with  $\nu = 240$ .

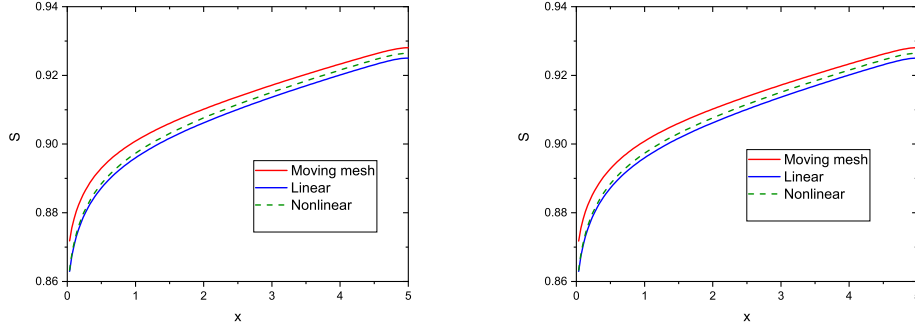


Figure 2.4:  $S(T)$  calculated by 3 experiments at  $T = 5000$ . The red curve is the height of  $S(T)$  computed by moving mesh. The blue curve is computed by the displacement  $\eta(T)$  with linear condition. The green dash curve is computed by the displacement  $\eta(T)$  with nonlinear condition. If the curve of moving mesh is regarded as the reference solution, it is easy to see that the nonlinear approximation does better than the linear approximation. Left figure corresponds to with  $\nu = 240$  and Right figure to  $\nu = 0.01$ .

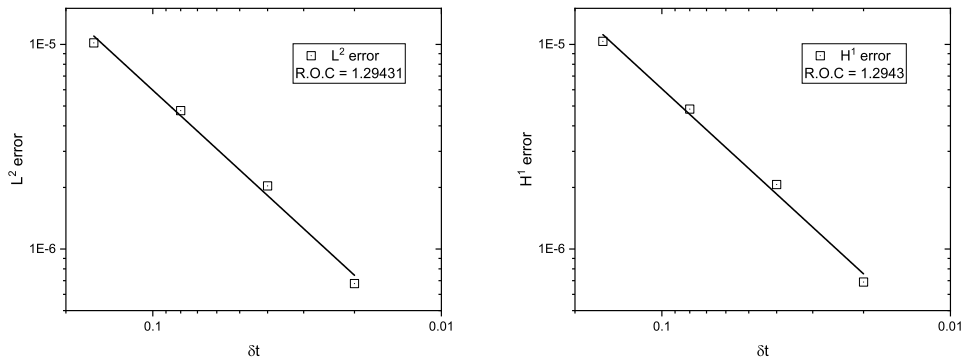


Figure 2.5:  $L^2$  relative error versus  $\delta t$  at  $T = 100$       Figure 2.6:  $H^1$  relative error versus  $\delta t$  at  $T = 100$ .

### 2.7.4 Numerical results at larger Reynolds number

In the previous example, where the values of the parameters correspond to the physical design of [61], we could have neglected the inertial terms and work with the Stokes approximation. In order to validate the algorithm at higher Reynolds number, which may be the case for other plating problems, we keep all parameters given in the end of Section 7.1 but change the Reynolds number to the inverse of  $\nu = 0.01$ . The same experiments are conducted as in Section 7.3. The numerical results obtained for the low Reynolds number and the larger Reynolds number are very similar; no visible changes can be seen (see the right side of Figure 2.4 ) so we do not display the plots of Figure 2.3 for the high Reynolds number case.

Furthermore, several numerical experiments show no visible change by choosing the Reynolds number between the inverse of 240 and the inverse of 0.01.

### 2.7.5 Influence of the term $\partial_t c$ in (2.19)

For the geometry considered in these numerical test no visible difference could be observed between (2.12) and (2.19) .

## 2.8 Conclusion

We have proposed a simplified model which approximates the Electroless process of [61] by replacing the time dependent domain occupied by the reacting chemical by a fixed domain using a transpiration approximation. We have validated the approximation numerically with a finite element method in space and a fully implicit in time approximation. We have constructed an existence proof by using variational convex analysis or fixed point arguments. The proof is technical and long because the nonlinearity is on the boundary condition and because it required a convexification of the energy potential and the maximum principle. However it was worth the effort because it gives a stable ground for the numerical studies and it may be useful for other similar problems. We plan to extend this study to two phase flows to take into account the formation of bubbles.

## 2.A Proof of Lemma 2.4.3.

Let  $\rho_1, \rho_2 \in W$ . Formula (2.41) gives

$$\begin{aligned} \langle A\rho_1 - A\rho_2, w \rangle &= \frac{1}{\delta t} \int_{\Omega} (\rho_1 - \rho_2) w dx \\ &+ \frac{1}{2} \int_{\Omega} [(\mathbf{u}^{m+1} \cdot \nabla(\rho_1 - \rho_2))w - (\mathbf{u}^{m+1} \cdot \nabla w)(\rho_1 - \rho_2)] dx + D \int_{\Omega} \nabla(\rho_1 - \rho_2) \cdot \nabla w dx \\ &+ \int_S (\phi_m(\rho_1 + \tilde{c}_{in}) - \phi_m(\rho_2 + \tilde{c}_{in}))w + \frac{1}{2} \int_{\Gamma_{out}} (\mathbf{u}^{m+1} \cdot \mathbf{n})(\rho_1 - \rho_2)w \end{aligned} \quad (2.97)$$

We estimate each term on the right hand side of (2.97):

$$\frac{1}{\delta t} \int_{\Omega} (\rho_1 - \rho_2) w dx \leq \frac{1}{\delta t} \|\rho_1 - \rho_2\|_0 \|w\|_0 \leq \frac{1}{\delta t} \|\rho_1 - \rho_2\|_1 \|w\|_1 \quad (2.98)$$

$$\begin{aligned} \int_{\Omega} (\mathbf{u}^{m+1} \cdot \nabla(\rho_1 - \rho_2)) w dx &\leq \|\mathbf{u}^{m+1}\|_{L^4(\Omega)} \|\nabla(\rho_1 - \rho_2)\|_0 \|w\|_{L^4(\Omega)} \\ &\leq C \|\mathbf{u}^{m+1}\|_1 \|\rho_1 - \rho_2\|_1 \|w\|_1 \end{aligned} \quad (2.99)$$

$$\begin{aligned} \int_{\Omega} (\mathbf{u}^{m+1} \cdot \nabla w)(\rho_1 - \rho_2) dx &\leq \|\mathbf{u}^{m+1}\|_{L^4(\Omega)} \|\nabla w\|_0 \|\rho_1 - \rho_2\|_{L^4(\Omega)} \\ &\leq C \|\mathbf{u}^{m+1}\|_1 \|\rho_1 - \rho_2\|_1 \|w\|_1 \end{aligned} \quad (2.100)$$

$$\int_{\Omega} \nabla(\rho_1 - \rho_2) \cdot \nabla w dx \leq \|\nabla(\rho_1 - \rho_2)\|_0 \|\nabla w\|_0 \leq \|\rho_1 - \rho_2\|_1 \|w\|_1 \quad (2.101)$$

Let  $x_1, x_2 \in \mathbb{R}$ . If  $x_1 + \tilde{c}_{in}$ , and  $x_2 + \tilde{c}_{in} > \frac{1}{2\alpha}$ , then  $|\bar{\psi}_{,c}(x_1 + \tilde{c}_{in}) - \bar{\psi}_{,c}(x_2 + \tilde{c}_{in})| = 0$ . If  $x_1 + \tilde{c}_{in} \leq \frac{1}{2\alpha}$  and  $x_2 + \tilde{c}_{in} > \frac{1}{2\alpha}$ , then

$$\begin{aligned} |\bar{\psi}_{,c}(x_1 + \tilde{c}_{in}) - \bar{\psi}_{,c}(x_2 + \tilde{c}_{in})| &\leq |\bar{\psi}_{,cc}(x_1 + \tilde{c}_{in})| |x_1 - x_2| \\ &\leq |1 - \alpha(x_1 + \tilde{c}_{in})| |x_1 - x_2| \leq (1 + \alpha + \alpha|x_1|) |x_1 - x_2|. \end{aligned}$$

If  $x_1 + \tilde{c}_{in}$ , and  $x_2 + \tilde{c}_{in} \leq \frac{1}{2\alpha}$ , then

$$\begin{aligned} |\bar{\psi}_{,c}(x_1 + \tilde{c}_{in}) - \bar{\psi}_{,c}(x_2 + \tilde{c}_{in})| &= |x_1 + \tilde{c}_{in} - \frac{\alpha}{2}(x_1 + \tilde{c}_{in})^2 - (x_2 + \tilde{c}_{in}) + \frac{\alpha}{2}(x_2 + \tilde{c}_{in})^2| \\ &= |x_1 - x_2 - \frac{\alpha}{2}(x_1 + \tilde{c}_{in})^2 + \frac{\alpha}{2}(x_2 + \tilde{c}_{in})^2| \\ &= |x_1 - x_2 - \frac{\alpha}{2}(x_1 + x_2)(x_1 - x_2) - \alpha\tilde{c}_{in}(x_1 - x_2)| \\ &\leq (1 + \alpha + \frac{\alpha}{2}|x_1| + \frac{\alpha}{2}|x_2|) |x_1 - x_2|. \end{aligned}$$

Now we can conclude that

$$\begin{aligned} \int_S (\bar{\psi}_{,c}(\rho_1 + \tilde{c}_{in}) - \bar{\psi}_{,c}(\rho_2 + \tilde{c}_{in})) w &\leq \int_S (1 + \alpha + \frac{\alpha}{2}|\rho_1| + \frac{\alpha}{2}|\rho_2|) |\rho_1 - \rho_2| |w| \\ &\leq (1 + \alpha) \|\rho_1 - \rho_2\|_S \|w\|_S + \frac{\alpha}{2} (\|\rho_1\|_{L^3(S)} + \|\rho_2\|_{L^3(S)}) \|\rho_1 - \rho_2\|_{L^3(S)} \|w\|_{L^3(S)} \\ &\leq C_1 \|\rho_1 - \rho_2\|_1 \|w\|_1 + C_2 (\|\rho_1\|_1 + \|\rho_2\|_1) \|\rho_1 - \rho_2\|_1 \|w\|_1. \end{aligned} \quad (2.102)$$

Now,

$$\begin{aligned} &\int_S \sum_{j=0}^m c^j \delta t ((\rho_1 + \tilde{c}_{in}) - (\rho_2 + \tilde{c}_{in})) w \\ &= \int_S \sum_{j=0}^m c^j \delta t (\rho_1 - \rho_2) w \leq \delta t \int_S \sum_{j=0}^m |c^j| |\rho_1 - \rho_2| |w| \\ &\leq \delta t \sum_{j=0}^m \|c^j\|_{L^3(S)} \|\rho_1 - \rho_2\|_{L^3(S)} \|w\|_{L^3(S)} \leq C \delta t \sum_{j=0}^m \|c^j\|_1 \|\rho_1 - \rho_2\|_1 \|w\|_1 \end{aligned} \quad (2.103)$$

And finally,

$$\begin{aligned} \int_{\Gamma_{out}} (\mathbf{u}^{m+1} \cdot \mathbf{n})(\rho_1 - \rho_2)w &\leq \int_{\Gamma_{out}} |\mathbf{u}^{m+1} \cdot \mathbf{n}| |\rho_1 - \rho_2| |w| \\ &\leq \|\mathbf{u}^{m+1}\|_{L^3(\Gamma_{out})} \|\rho_1 - \rho_2\|_{L^3(\Gamma_{out})} \|w\|_{L^3(\Gamma_{out})} \leq C \|\mathbf{u}^{m+1}\|_1 \|\rho_1 - \rho_2\|_1 \|w\|_1 \end{aligned} \quad (2.104)$$

Combining (2.98)-(2.104), we have

$$\begin{aligned} &|\langle A\rho_1 - A\rho_2, w \rangle| \\ &\leq \left( C_1 + C_2 \|\mathbf{u}^{m+1}\|_1 + C_3 (\|\rho_1\|_1 + \|\rho_2\|_1) + C_4 \delta t \sum_{j=0}^m \|c^j\|_1 \right) \|\rho_1 - \rho_2\|_1 \|w\|_1 \end{aligned} \quad (2.105)$$

This completes the proof. Q.E.D.

## 2.B Error estimates

In this section, we further assume that

$$\begin{aligned} \text{(A1)} \quad &\int_0^T \|\partial_{tt} c\|_{-1}^2 dt \leq M_1 \quad \text{for some constant } M_1 \text{ and} \\ \text{(A2)} \quad &\sup_{t \in [0, T]} \|\partial_t c\|_{H^1(\Omega)'} < M_2 \quad \text{for some constant } M_2. \end{aligned} \quad (2.106)$$

For convenience, we define

$$\begin{aligned} B(u, v) &:= \left(1 + \frac{\alpha i_0^2}{D} u\right) i_0 v, \\ b(u, v, w) &:= \int_S \left(1 + \frac{\alpha i_0^2}{D} u\right) i_0 v w, \\ G(u, v, w) &:= \int_S \frac{\alpha i_0^3}{D} u v w. \end{aligned} \quad (2.107)$$

The difference equation for the exact solution of  $c$  defined by (2.5) can be expressed as:

$$\frac{c(t^{m+1}) - c(t^m)}{\delta t} + \mathbf{u}^{m+1} \cdot \nabla c(t^{m+1}) - D \Delta c(t^{m+1}) = R^m, \quad (2.108)$$

where

$$R^m = \frac{1}{\delta t} \int_{t^m}^{t^{m+1}} (t - t^m) \partial_{tt} c(t) dt \quad (2.109)$$

Defining  $\epsilon^j = c(t^j) - c^j$ , the error equation can be expressed by

$$\frac{\epsilon^{m+1} - \epsilon^m}{\delta t} + \mathbf{u}^{m+1} \cdot \nabla \epsilon^{m+1} - D \Delta \epsilon^{m+1} = R^m \quad (2.110)$$

subject to the boundary condition

$$\begin{aligned} \epsilon^{m+1} &= 0 \quad \text{on } \Gamma_{in}, \quad \frac{\partial \epsilon^{m+1}}{\partial n} = 0 \quad \text{on } \Gamma_{wall} \cup \Gamma_{out} \\ D \frac{\partial \epsilon^{m+1}}{\partial n} + B \left( \int_0^{t^{m+1}} c(s) ds, c(t^{m+1}) \right) - B \left( \sum_{j=0}^m c_j \delta t, c^{m+1} \right) &= 0 \quad \text{on } S. \end{aligned} \quad (2.111)$$

The symmetrized weak formulation to (2.108) is

$$\begin{aligned} & \int_{\Omega} \frac{c(t^{m+1}) - c(t^m)}{\delta t} w + D \int_{\Omega} \nabla c(t^{m+1}) \cdot \nabla w \\ & + \frac{1}{2} \int_{\Omega} [(\mathbf{u}^{m+1} \cdot \nabla c(t^{m+1}))w - (\mathbf{u}^{m+1} \cdot \nabla w)c(t^{m+1})] dx + \int_{\Gamma_{out}} (\mathbf{u}^{m+1} \cdot \mathbf{n}) c^{m+1} w \\ & + \int_S \left( 1 - \frac{\alpha c^{m+1}}{2} + \frac{\alpha i_0^2}{D} \sum_{j=0}^m c^j \right) i_0 c^{m+1} w = \int_{\Omega} R^m w dx \end{aligned} \quad (2.112)$$

Subtracting (2.112) by (2.35), we have

$$\begin{aligned} & \int_{\Omega} \frac{\epsilon^{m+1} - \epsilon^m}{\delta t} w dx + D \int_{\Omega} \nabla \epsilon^{m+1} \cdot \nabla w dx \\ & + \frac{1}{2} \int_{\Omega} [(\mathbf{u}^{m+1} \cdot \nabla \epsilon^{m+1})w - (\mathbf{u}^{m+1} \cdot \nabla w)\epsilon^{m+1}] dx + \int_{\Gamma_{out}} (\mathbf{u}^{m+1} \cdot \mathbf{n}) \epsilon^{m+1} w \\ & - \int_S \frac{\alpha i_0}{2} (c(t^{m+1}) + c^m) \epsilon^{m+1} w + b \left( \int_0^{t^{m+1}} c(s) ds, c(t^{m+1}), w \right) \\ & - b \left( \sum_{j=0}^m c^j \delta t, c^{m+1}, w \right) = \int_{\Omega} R^m w dx \end{aligned} \quad (2.113)$$

Before investigating the error estimate, some auxiliary results are needed. We collect them in the Remark below:

**Remark 2.B.1** We have

$$\begin{aligned} & B \left( \int_0^{t^{m+1}} c(s) ds, c(t^{m+1}) \right) - B \left( \sum_{j=0}^m c^j \delta t, c^{m+1} \right) \\ & = \left( 1 + \frac{\alpha i_0^2}{D} \sum_{j=0}^m c^j \delta t \right) i_0 \epsilon^{m+1} + \frac{\alpha i_0^3}{D} \left[ \int_0^{t^{m+1}} c(s) ds - \sum_{j=0}^m c^j \delta t \right] c(t^{m+1}) \end{aligned} \quad (2.114)$$

Defining

$$\xi^m = \int_0^{t^{m+1}} c(s) ds - \sum_{j=0}^m c^j \delta t \quad (2.115)$$

we have

$$\xi^m = \sum_{j=0}^m \epsilon^j \delta t + \phi^m, \quad (2.116)$$



where  $\phi^m = \sum_{j=0}^m \partial_t c(\theta^j) \delta t^2$  for some  $\theta^j \in (t^j, t^{j+1})$ . By (2.114), (2.115), (2.116) and letting  $w = \epsilon^{m+1}$  in (2.113), we have

$$\begin{aligned} & \frac{1}{\delta t} \|\epsilon^{m+1}\|^2 - \frac{1}{\delta t} \int_{\Omega} \epsilon^{m+1} \epsilon^m dx + D \|\nabla \epsilon^{m+1}\|^2 + b \left( \sum_{j=0}^m c^j \delta t, \epsilon^{m+1}, \epsilon^{m+1} \right) \\ & + G(c(t^{m+1}), \sum_{j=0}^m \epsilon^j \delta t, \epsilon^{m+1}) + G(c(t^{m+1}), \phi^m, \epsilon^{m+1}) + \int_{\Gamma_{out}} (\mathbf{u}^{m+1} \cdot \mathbf{n}) (\epsilon^{m+1})^2 \\ & - \int_S \frac{\alpha i_0}{2} (c(t^{m+1}) + c^{m+1}) (\epsilon^{m+1})^2 = \int_{\Omega} R^m w dx \end{aligned} \quad (2.117)$$

Multiplying the both sides by  $\delta t$ , we get

$$\begin{aligned} & \|\epsilon^{m+1}\|^2 + D \delta t \|\nabla \epsilon^{m+1}\|^2 + \delta t b \left( \sum_{j=0}^m c^j \delta t, \epsilon^{m+1}, \epsilon^{m+1} \right) \\ & + \delta t G(c(t^{m+1}), \sum_{j=0}^m \epsilon^j \delta t, \epsilon^{m+1}) + \delta t G(c(t^{m+1}), \phi^m, \epsilon^{m+1}) + \delta t \int_{\Gamma_{out}} (\mathbf{u}^{m+1} \cdot \mathbf{n}) (\epsilon^{m+1})^2 \\ & - \delta t \int_S \frac{\alpha i_0}{2} (c(t^{m+1}) + c^{m+1}) (\epsilon^{m+1})^2 = \delta t \int_{\Omega} R^m w dx + \int_{\Omega} \epsilon^{m+1} \epsilon^m dx \end{aligned} \quad (2.118)$$

Q.E.D.

**Theorem 2.B.1** There is a generic constant  $C$  such that

$$\|\epsilon^{m+1}\| \leq C \delta t \quad \forall 0 \leq m \leq \frac{T}{\delta t} - 1 \quad (2.119)$$

and

$$\|\epsilon^{m+1}\|_1 \leq C \delta t^{\frac{1}{2}} \quad \forall 0 \leq m \leq \frac{T}{\delta t} - 1. \quad (2.120)$$

*Proof.* By a recurrence argument, we are going to show that if the statements (2.119) and (2.120) hold simultaneously for all  $\epsilon^j$  and for all  $j \leq m$ , then they hold as well for  $\epsilon^{m+1}$ . Notice that it is true when  $m = 0$ .

Defining  $G_1 = |G(c(t^{m+1}), \sum_{j=0}^m \epsilon^j \delta t, \epsilon^{m+1})|$  and  $G_2 = |G(c(t^{m+1}), \phi^m, \epsilon^{m+1})|$ , we have the estimates:

$$\begin{aligned} G_1 & \leq \frac{\alpha i_0^3}{D} \sum_{j=0}^m \int_S |c(t^{m+1}) \epsilon^j \epsilon^{m+1} \delta t| \\ & \leq \frac{\alpha i_0^3}{D} \sum_{j=0}^m \int_S |\delta t \epsilon^j \epsilon^{m+1}| \leq \frac{\alpha i_0^3}{D} \left( \sum_{j=0}^m \|\epsilon^j\|_S \delta t \right) \|\epsilon^{m+1}\|_S \\ & \leq C \left( \sum_{j=0}^m \|\epsilon^j\|_1 \delta t \right) \|\epsilon^{m+1}\|_1 \leq C(m+1) \delta t^{\frac{3}{2}} \|\epsilon^{m+1}\|_1 \leq C \|\epsilon^{m+1}\| \delta t^{\frac{1}{2}}. \end{aligned} \quad (2.121)$$

Using (A2), we have

$$\begin{aligned} G_2 &\leq \frac{\alpha i_0^3}{D} \int_S |c(t^{m+1}) \phi^m \epsilon^{m+1}| \leq \frac{\alpha i_0^3}{D} \int_S |\phi^m \epsilon^{m+1}| \\ &\leq \frac{\alpha i_0^3}{D} \|\phi^m\|_S \|\epsilon^{m+1}\|_S \leq C \|\phi^m\|_1 \|\epsilon^{m+1}\|_1 \leq C \delta t^2 \|\epsilon^{m+1}\|_1. \end{aligned} \quad (2.122)$$

By (A1), we have

$$\begin{aligned} &\delta t \left| \int_{\Omega} R^m \epsilon^{m+1} dx \right| \\ &\leq \frac{D}{4} \delta t \|\epsilon^{m+1}\|_1^2 + C \delta t^{-1} \|R^m\|_{H^1(\Omega)'}^2 \\ &= \frac{D}{4} \|\epsilon^{m+1}\|_1^2 + C \delta t^{-1} \left\| \int_{t^m}^{t^{m+1}} (t - t^m) \partial_{tt} c dt \right\|_{H^1(\Omega)'}^2 \\ &\leq \frac{D}{4} \|\epsilon^{m+1}\|_1^2 + C \delta t^{-1} \int_{t^m}^{t^{m+1}} \|\partial_{tt} c\|_{H^1(\Omega)'}^2 dt \int_{t^m}^{t^{m+1}} (t - t^m)^2 dt \\ &\leq \frac{D}{4} \|\epsilon^{m+1}\|_1^2 + C \delta t^2 \int_{t^m}^{t^{m+1}} \|\partial_{tt} c\|_{H^1(\Omega)'}^2 dt \\ &\leq \frac{D}{4} \|\epsilon^{m+1}\|_1^2 + C \delta t^2 \end{aligned} \quad (2.123)$$

$$\begin{aligned} &b\left(\sum_{j=0}^m c^j \delta t, \epsilon^{m+1}, \epsilon^{m+1}\right) - \int_S \frac{\alpha i_0}{2} (c(t^{m+1}) + c^{m+1}) (\epsilon^{m+1})^2 \\ &\geq \int_S \left(1 + \frac{\alpha i_0^2}{D} \sum_{j=0}^m c^j \delta t\right) i_0 (\epsilon^{m+1})^2 - \int_S \alpha i_0 (\epsilon^{m+1})^2 \\ &\geq \int_S \left((1 - \alpha) + \frac{\alpha i_0^2}{D} \sum_{j=0}^m c^j \delta t\right) i_0 (\epsilon^{m+1})^2 \geq 0. \end{aligned} \quad (2.124)$$

$$\int_{\Omega} \epsilon^{m+1} \epsilon^m dx \leq \frac{1}{2} \|\epsilon^m\|^2 + \frac{1}{2} \|\epsilon^{m+1}\|^2. \quad (2.125)$$

Combining (2.118), (2.121)-(2.125), and since the boundary term of  $\Gamma_{out}$  in (2.118) is nonnegative, we have

$$\left(\frac{1}{2} - \frac{1}{4} D \delta t\right) \|\epsilon^{m+1}\|^2 + \frac{3}{4} D \delta t \|\epsilon^{m+1}\|_1^2 \leq C \|\epsilon^{m+1}\|_1 \delta t^{\frac{3}{2}} + C \delta t^2. \quad (2.126)$$

This implies (2.120). Now using (2.126) and (2.120), we get (2.119). Q.E.D.

**Theorem 2.B.2 (Improved estimate)** For  $0 \leq m \leq \frac{T}{\delta t} - 1$ , we have

$$\delta t \sum_{j=0}^m \|\epsilon^{j+1}\|_1^2 \leq C \delta t^2 \quad (2.127)$$

*Proof.* Putting  $w = 2\epsilon^{m+1}$  in (2.118) and using the estimates in Theorem 2.B.1, we have

$$\begin{aligned} \|\epsilon^{m+1}\|^2 + 2D\delta t \|\nabla \epsilon^{m+1}\|^2 &\leq 2\delta t C_1 \|\epsilon^{m+1}\|_1 \left( \sum_{j=0}^m \|\epsilon^j\|_1 \delta t \right) \\ &+ 2C_2 \delta t^3 \|\epsilon^{m+1}\|_1 + \frac{D}{4} \delta t \|\epsilon^{m+1}\|_1^2 + C_3 \delta t^2 \int_{t^m}^{t^{m+1}} \|\partial_{tt} c\|_{H^1(\Omega)'}^2 dt + \|\epsilon^m\|^2 \end{aligned} \quad (2.128)$$

Note that

$$\|\epsilon^{m+1}\|^2 + 2D\delta t \|\epsilon^{m+1}\|_1^2 = (1 - 2D\delta t) \|\epsilon^{m+1}\|^2 + 2D\delta t \|\epsilon^{m+1}\|_1^2.$$

Taking the sum of (2.128) from 0 to  $m$  and using (A1), we have

$$\begin{aligned} (1 - \frac{9}{4} D\delta t) \|\epsilon^{m+1}\|^2 + \frac{7}{4} \sum_{j=0}^m D\delta t \|\epsilon^{j+1}\|_1^2 &\leq \sum_{j=0}^m 2\delta t C_1 \|\epsilon^{j+1}\|_1 \left( \sum_{k=0}^j \|\epsilon^k\|_1 \delta t \right) \\ &+ \sum_{j=0}^m 2C_2 \delta t^3 \|\epsilon^{j+1}\|_1 + C_3 \delta t^2. \end{aligned} \quad (2.129)$$

The first term on the right hand side of (2.129) can be estimated by

$$\begin{aligned} &\sum_{j=0}^m 2\delta t C_1 \|\epsilon^{j+1}\|_1 \left( \sum_{k=0}^j \|\epsilon^k\|_1 \delta t \right) \\ &\leq \sum_{j=0}^m \frac{D}{4} \delta t \|\epsilon^{j+1}\|_1^2 + C\delta t^2 \sum_{j=0}^m \sum_{k=0}^j \|\epsilon^k\|_1^2 \\ &\leq \frac{D}{4} \delta t \|\epsilon^{m+1}\|_1^2 + C\delta t \sum_{j=0}^m \|\epsilon^j\|_1^2. \end{aligned} \quad (2.130)$$

Similarly, the second term can be estimated by

$$\begin{aligned} \sum_{j=0}^m 2C_2 \delta t^3 \|\epsilon^{j+1}\|_1 &\leq \sum_{j=0}^m 2C\delta t^3 \left( \frac{1}{2\nu} \|\epsilon^{m+1}\|_1^2 + \frac{\nu}{2} |\Omega| \right) \\ &\leq \nu C T |\Omega| \delta t^2 + \frac{C}{\nu} \delta t^2 \sum_{j=0}^m \|\epsilon^{j+1}\|_1^2 \\ &\leq C\delta t^2 + \frac{D}{4} \delta t \sum_{j=0}^m \|\epsilon^j\|_1^2 + \frac{D}{4} \delta t \|\epsilon^{m+1}\|_1^2 \end{aligned} \quad (2.131)$$

for every  $\nu > 0$ .

Finally, employing (2.129)-(2.131), we have

$$\left( 1 - \frac{11}{4} D\delta t \right) \|\epsilon^{m+1}\|^2 + \frac{5}{4} D\delta t \sum_{j=0}^m \|\epsilon^{j+1}\|_1^2 \leq C_1 \delta t^2 + C_2 \delta t \sum_{j=0}^m \|\epsilon^j\|_1^2. \quad (2.132)$$

By induction on  $m$ , we can easily show that

$$\frac{5}{4}D\delta t \sum_{j=0}^m \|\epsilon^{j+1}\|_1^2 \leq C\delta t^2. \quad (2.133)$$

Q.E.D.



## Chapter 3

# Simulation on electroless plating problem with gas generation

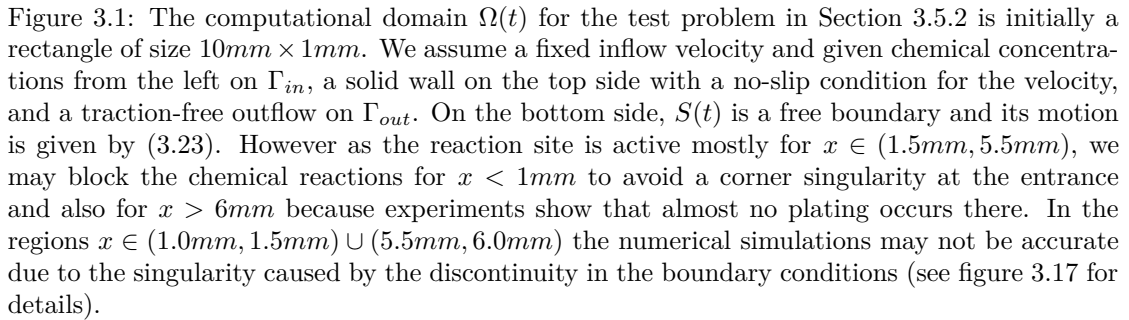
### 3.1 Introduction

When emphasizing on micro-scale electroless plating problem, gas generation will be a serious issue. The existence of relatively large bubbles in a microchannel has been an important issue in the study of microfluid[76, 57, 129]. In electroless plating process, the bubbles may prevent electrolyte from going into the region needed to be plated. In view of the trouble caused by bubble generation, we are motivated to understand the mechanism of bubble motion and bubble generation in electroless process. From a theoretical point of view, the physical phenomena for describing electroless process are very complicated. In practical simulation, not all the physical phenomena are of interest. Therefore, for the simulation, we chose a system which includes: gas-liquid two phase flow, chemical species transport, surface reaction, and moving boundary caused by deposition.

Numerous papers about modeling and simulation of gas-liquid two phase flow have been published [116, 115, 2, 33, 45]. In terms of how we resolve the motion of the gaseous phase flows, the working models in most of these papers can be sorted into two classes: (i) phase field or level set models where the gas-liquid interface is tracked[1, 107, 112, 90]; (ii) averaged models [63, 134, 41]. Several reasons support our choice for an averaged model: (i) The bubble generation is random, we only know that there is a higher chance of gas generation occurring in regions of higher concentration of dissolving gas; (ii) Even if the bubble generation can be well predicted, vast amounts of bubbles are generated in a short moment for electroless process; furthermore, the computational cost for capturing each bubble is prohibitive; (iii) Interfacial terms (e.g. terms caused by phase change) can be easily estimated if the averaged model is applied (see Appendix A); (iv) it simplifies substantially the modeling.

Experimentally, the bubbles are seen to get stuck somewhere in the microchannel. This indicates that the velocities of two phases are quite different. To allow a disparity of motion between the liquid phase and gaseous phase, a two velocities model will be used. To our knowledge, such approach is new for incompressible two phase flows in thin microchannels.

A system of linear convection-diffusion equations with additional phase change terms is applied for depicting the concentration profiles of chemical species. We use the mixed potential theory (see for instance [74]) to model the reaction boundary condition describing the electroless process, which is a Robin boundary condition subject to electron balance constraints. We further



For numerical simulations, the Galerkin characteristic method[98] is applied for time discretization. The Finite element method of degree one is used for space discretization. The well-posedness of the numerical scheme for the coupling system is proved. We reproduce a one-dimensional numerical simulation on electroless nickel plating problem to compare with [66]. The numerical code for the full system is implemented as well and we compare the numerical results with a real-world experiment done by one of the authors for this purpose. Unfortunately the numerical experiment is very difficult to make and it gave only qualitative results. So the numerical results are compared qualitatively only with the experiment.

### 3.2 Modeling equations for liquid-gas flow

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WORK IN PROGRESS AS OF FEBRUARY 5, 2022

### 3.2.1 Volume averaging

We review the derivation proposed by Ni and Beckermann [85].

Let  $\Omega_0(x, t)$  be an small open set to be observed in  $\Omega(t)$  and  $\Omega_k \subset \Omega_0$  the set occupied by phase  $k$  and bounded by the interface  $\partial\Omega_k$ , which is assumed to be oriented. Assume that  $\cup_k \Omega_k = \Omega_0$  and  $\Omega_k \cap \Omega_j = \emptyset$ ,  $k \neq j$ . Let  $\mathbf{n}_k$  be a outer normal to  $\partial\Omega_k$  and  $\mathbf{w}_k$  the normal velocity of  $\partial\Omega_k$ .

Let  $\Psi$  be a function of a slow variable  $x$  and a fast variable  $y$  due to the phase change. The volume average of  $\Psi$  in phase  $k$  is  $\langle \Psi \rangle_k(x, t) = \frac{1}{V_0} \int_{\Omega_0(x, t)} \chi_k(y) \Psi(x, y) dy$ , where  $\chi_k$  is the indicator function of the domain of phase  $k$  and  $V_0 = \int_{\Omega_0} dx$ , assumed constant. The intrinsic volume average is defined as

$$\langle \Psi \rangle_k^{(k)} = \frac{V_0}{V_k} \langle \Psi \rangle_k \quad \text{where } V_k = \int_{\Omega_0} \chi_k dy \quad (3.1)$$

The volume fraction  $r_k = \frac{V_k}{V_0}$  has the properties  $\sum_k r_k = 1$  and  $\langle \Psi \rangle_k = r_k \langle \Psi \rangle_k^{(k)}$ . Some useful formulas in terms of the averaging are listed below [123, 109]:

$$\left\langle \frac{\partial \Psi}{\partial t} \right\rangle_k = \frac{\partial \langle \Psi \rangle_k}{\partial t} - \frac{1}{V_0} \int_{\partial\Omega_k} \Psi_k \mathbf{w}_k \cdot \mathbf{n}_k dA, \quad \langle \nabla \Psi \rangle_k = \nabla \langle \Psi \rangle_k + \frac{1}{V_0} \int_{\partial\Omega_k} \Psi_k \mathbf{n}_k dA. \quad (3.2)$$

In principle one should introduce also fast and slow time variables but it is assumed that spatially averaged functions are no longer varying fast in time.

### 3.2.2 Mass conservation

We consider a gas and a liquid phase. Let  $\rho_g$  be the density of gas,  $\rho_l$  the density of liquid. We have the mass conservation for both phases ( $l$  for liquid and  $g$  for gas):

$$\partial_t(r_j \rho_j) + \nabla \cdot (r_j \rho_j \mathbf{u}_j) = \dot{S}_j, \quad l = l, g \quad (3.3)$$

where  $\dot{S}_g$  is the mass gained owing to the precipitation of dissolved gas,  $\dot{S}_l$  is the mass loss when liquid is replaced by the gas, and  $\mathbf{u}_g(x, t)$ ,  $\mathbf{u}_l(x, t)$  are the volume averaged fluid flow of gas and liquid, respectively. Since the mass gained in gas balances the mass loss in liquid, we have

$$\dot{S}_g = -\dot{S}_l. \quad (3.4)$$

For chemical species, we assume that the ions are transported only by the liquid electrolyte. Let  $c_s$  be the volume averaged concentration of metallic ions destined to be deposited on the reacting surface,  $c_g$  the volume averaged concentration of dissolved gas and  $c_k$ ,  $k = k_1, \dots, k_M$  the volume averaged concentration of other chemical species participating to the chemical reaction. The equations for the concentrations are

$$\partial_t(r_l \rho_l c_j) + \nabla \cdot (r_l \rho_l c_j \mathbf{u}_l) - \nabla \cdot (r_l \rho_l D_j \nabla c_j) - G_j = 0, \quad j = s, g, k. \quad (3.5)$$

where  $G_j$ ,  $j = s, k$  are interfacial terms due to the phase change. By (3.3), we can rewrite the above equation by

$$r_l \rho_l (\partial_t c_j + \mathbf{u}_l \cdot \nabla c_j) - \nabla \cdot (r_l \rho_l D_j \nabla c_j) - G_j + \dot{S}_l c_j = 0, \quad j = s, g, k. \quad (3.6)$$



where  $D_j$  are the diffusion coefficients. In particular, since the gas is consumed by the phase change, we have

$$G_g = -\frac{1}{V_0} \int_{\partial\Omega_l} \rho_l c_g (\mathbf{u}_l - \mathbf{w}_l) \cdot \mathbf{n}_l dA - \rho_l M_g K r_l (c_g - c_{sat})^+ \quad (3.7)$$

by assuming the gas precipitation is linearly dependent on the dissolving gas concentration[87, 120].

In the above,  $\mathbf{w}_l$  is the interface velocity of  $\partial\Omega_l$  and where  $K$  is a constant independent of  $r_g$ ,  $r_l$  and  $c_{sat}$  is the saturated concentration of the gas,  $M_g$  is the reciprocal of the molar mass of the gas,

$$\dot{S}_g = K r_l (c_g - c_{sat})^+. \quad (3.8)$$

Moreover,  $G_j$ ,  $j = s, k, g$  can be estimated by (see Appendix A)

$$G_j \approx \dot{S}_l c_j, \quad j = s, k, \quad G_g \approx \dot{S}_l c_g - \rho_l M_g K r_l (c_g - c_{sat})^+. \quad (3.9)$$

For incompressible fluids, a volume conservation is derived from (3.3):

$$\sum_{\alpha=g,l} \frac{1}{\rho_\alpha} \left[ \partial_t (r_\alpha \rho_\alpha) + \nabla \cdot (r_\alpha \rho_\alpha \mathbf{u}_\alpha) - \dot{S}_\alpha \right] = 0. \quad (3.10)$$

By (3.4), the above reduces to

$$\nabla \cdot (r_g \mathbf{u}_g + r_l \mathbf{u}_l) = \dot{S}_g \left( \frac{1}{\rho_g} - \frac{1}{\rho_l} \right). \quad (3.11)$$

Recall that the physical domain is occupied either by gas or liquid, therefore  $r_g(t) + r_l(t) = 1$  at all times.

### 3.2.3 Equations of motion

Let  $\mu_g$ ,  $\mu_l$  be the viscosity of the gas and the liquid, respectively. The volume averaged Navier-Stokes equations are used for momentum balance (see [85]):

$$\partial_t (r_j \rho_j \mathbf{u}_j) + \nabla \cdot (r_j \rho_j \mathbf{u}_j \otimes \mathbf{u}_j) + r_j \nabla p_j - \mu_j \nabla \cdot (r_j D(\mathbf{u}_j)) + M_{D,j} = \mathbf{F}_j, \quad j = g, l \quad (3.12)$$

where  $p_j$ ,  $M_{D,j}$ ,  $\mathbf{F}_j$ ,  $j = l, g$  are pressure, drag force terms[41, 85]

$$\begin{aligned} M_{D,g} &= C_D r_g |\mathbf{u}_g - \mathbf{u}_l| (\mathbf{u}_g - \mathbf{u}_l) \\ M_{D,l} &= C_D r_g |\mathbf{u}_g - \mathbf{u}_l| (\mathbf{u}_l - \mathbf{u}_g), \end{aligned} \quad (3.13)$$

where  $C_D$  is drag coefficient, and interfacial terms  $\mathbf{F}_j = -\frac{1}{V_0} \int_{\partial\Omega_j} \rho_j \mathbf{u}_j (\mathbf{u}_j - \mathbf{w}_j) \cdot \mathbf{n}_j dA$ ,  $j = l, g$ ,  $D(\mathbf{v}) = \nabla \mathbf{v} + (\nabla \mathbf{v})^T$  is the viscous stress tensor for any vector-valued function  $\mathbf{v}$ ;  $\mathbf{F}_j$ ,  $j = l, g$  can be estimated by (see Appendix A)

$$\mathbf{F}_g \approx \dot{S}_g \mathbf{u}_g, \quad \mathbf{F}_l \approx \dot{S}_l \mathbf{u}_l, \quad (3.14)$$

In view of (3.11), following [18, 19], we assume a constitutive relation  $p = p_l = p_g$  in order to close the system of equations. The velocity fields of both phases are assumed to be 0 outside

their own single phase region, respectively. Consequently, and by (3.3), (3.12), the momentum equations simplify to

$$r_j \rho_j (\partial_t \mathbf{u}_j + (\mathbf{u}_j \cdot \nabla) \mathbf{u}_j) + r_j \nabla p - \mu_j \nabla \cdot (r_j D(\mathbf{u}_j)) + \gamma_j C_D r_g |\mathbf{u}_g - \mathbf{u}_l| (\mathbf{u}_g - \mathbf{u}_l) = 0, \quad (3.15)$$

$$j = g, l, \quad \text{with } \gamma_g = 1 \text{ and } \gamma_l = -1$$

### 3.2.4 Boundary conditions

We consider a fluid flow from an input boundary  $\Gamma_{in}$  to an output boundary  $\Gamma_{out}$  with a solid wall at the bottom,  $\Gamma_{wall}$ :

$$\begin{aligned} \mathbf{u}_j &= \mathbf{u}_{in} \quad \text{on } \Gamma_{in}, \quad \mathbf{u}_j = 0 \quad \text{on } \Gamma_{wall}, \\ -\mu_j D(\mathbf{u}_j) \cdot \mathbf{n} + p \mathbf{n} &= 0 \quad \text{on } \Gamma_{out}, \quad j = l, g. \end{aligned} \quad (3.16)$$

The boundary conditions for  $r_j$ ,  $j = g, l$  are

$$\begin{aligned} r_g &= \epsilon, \quad r_l = 1 - \epsilon \quad \text{on } \Gamma_{in}, \\ \frac{\partial r_g}{\partial n} &= \frac{\partial r_l}{\partial n} = 0 \quad \text{on } \partial\Omega \setminus \Gamma_{in}, \end{aligned} \quad (3.17)$$

where  $\epsilon$  is a fixed positive small constant.

The boundary conditions for the concentrations of chemical species are, with  $c_{j,in}$  given:

$$c_j = c_{j,in} \quad \text{on } \Gamma_{in}, \quad \frac{\partial c_j}{\partial n} = 0 \quad \text{on } \Gamma_{wall} \cup \Gamma_{out}, \quad j = s, g, k \quad (3.18)$$

With  $F$  the Faraday constant, and  $z$  the atomic number of the material.

Referring to Figure 3.2, if  $S(t)$  is the reaction surface, we denote  $S_l(t) \subset S(t)$  the region occupied by the liquid and  $S_g(t) := S(t) \setminus S_l(t)$  the region occupied by gas. Choosing an arbitrary subset  $W \subset S(t)$ , the surface reaction takes place only on  $W \cap S_l(t)$ . Assuming that the concentration profile is uniform near the small region  $W$ , we have:  $-\int_W \rho_l D_j \frac{\partial c_j}{\partial n} dA = \int_{W \cap S_l(t)} \rho_l \frac{|I_j|}{z_j F} dA$ . Therefore by dividing both sides by  $\int_W 1 dA$ :

$$-D_j \frac{\partial c_j}{\partial n} = \frac{|I_j|}{z_j F}, \quad j = s, k, \quad -D_g \frac{\partial c_g}{\partial n} = -\frac{\beta |I_s|}{z_s F} \quad (3.19)$$

for a positive number  $\beta$  indicating the chemical equivalence for gaseous molecular generation.

In the above,  $I_j$  is the current density satisfying the Butler-Volmer equation

$$I_j = i_j(E_{mix}) c_j^{\kappa_j} := L_j \left[ \exp \left( \frac{\alpha_j z_j F (E_{mix} - E_j)}{R\theta} \right) - \exp \left( \frac{-\beta_j z_j F (E_{mix} - E_j)}{R\theta} \right) \right] c_j^{\kappa_j}, \quad j = s, k, \quad (3.20)$$

where  $R$  is the gas constant,  $E_j$  are the chemical potentials of species  $j$ ,  $\theta$  is the temperature,  $\alpha_j, \beta_j, L_j, \kappa_j$  are constants,  $E_{mix}$  is given by writing electrical neutrality :

$$I_s + \sum_k I_k = 0. \quad (3.21)$$

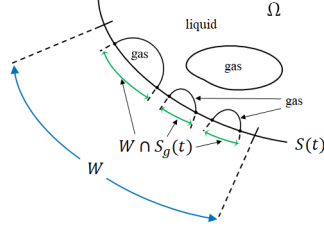


Figure 3.2: The reaction surface.

On  $S(t)$ , the fluid velocity induced by the deposition is

$$\mathbf{u}_g = \mathbf{u}_l = \frac{r_l V_s |I_s|}{z_s F} \mathbf{n}. \quad (3.22)$$

where  $V_s$  is a constant. Hence  $S(t)$  moves according to

$$\dot{x}(t) = (\mathbf{u}_g \cdot \mathbf{n})|_{x(t)}, \quad x(t) \in S(t) \quad (3.23)$$

### 3.2.5 Single phase flow

If there is no gaseous phase in the system and no dissolved gas in liquid, i.e.  $r_g = c_g = 0$ , then  $\mathbf{u} = \mathbf{u}_l$  and  $\dot{S}_g = 0$  and mass conservation reduces to  $\nabla \cdot \mathbf{u} = 0$ . The convection-diffusion of chemicals become,

$$\partial_t c_j + \mathbf{u} \cdot \nabla c_j - D_j \Delta c_j = 0, \quad j = s, k, \quad (3.24)$$

and the fluid system reduce to the Navier-Stokes equations:

$$\rho_l (\partial_t \mathbf{u} + (\mathbf{u} \cdot \nabla) \mathbf{u}) - \mu_l \Delta \mathbf{u} + \nabla p = 0, \quad \nabla \cdot \mathbf{u} = 0. \quad (3.25)$$

The above system of equations exactly describes the chemical species transported by the fluid flow satisfying the incompressible Navier-Stokes equation.

## 3.3 Numerical method

### 3.3.1 Notations

If  $f \in \mathbb{R}$ , we denote by  $f^+ := \max(f, 0)$  and by  $f^- := -\min(f, 0)$ . We denote by  $\|\cdot\|_{L^p} := \|\cdot\|_{L^p(\Omega(t))}$  the  $L^p$  norm on  $\Omega(t)$ ,  $\|\cdot\|_{W^{k,p}} := \|\cdot\|_{W^{k,p}(\Omega(t))}$  the  $W^{k,p}$  norm on  $\Omega(t)$ , and  $\|\cdot\|_{H^k} = \|\cdot\|_{W^{k,2}}$ ,  $0 \leq k \leq +\infty$ ,  $1 \leq p \leq +\infty$ . Remembering that  $c_k(x, t)$  is a vector, let us denote  $C = (c_s, c_k^T, c_g)^T$ .

We assume the densities  $\rho_j$  constant and denote  $\alpha_j = r_j \rho_j$  and the kinematic viscosities  $\nu_j = \mu_j / \rho_j$ . The system is

$$\partial_t \alpha_j + \mathbf{u}_j \cdot \nabla \alpha_j + \alpha_j \nabla \cdot \mathbf{u}_j - \alpha_l \frac{\gamma_j K}{\rho_l} (c_g - c_{sat})^+ = 0, \quad j = l, g \quad (3.26)$$

$$\alpha_j (\partial_t \mathbf{u}_j + \mathbf{u}_j \cdot \nabla \mathbf{u}_j + \rho_j^{-1} \nabla p) - \nu_j \nabla \cdot (\alpha_j D(\mathbf{u}_j)) + \gamma_j C_D r_g |\mathbf{u}_g - \mathbf{u}_l| (\mathbf{u}_g - \mathbf{u}_l) = 0, \quad j = g, l \quad (3.27)$$

$$\alpha_l(\partial_t C + \mathbf{u}_l \cdot \nabla C) - \nabla \cdot (\alpha_l \mathbf{D} \cdot \nabla C) + (0, 0, M_g K \alpha_l (c_g - c_{sat})^+)^T = 0, \quad (3.28)$$

where  $\mathbf{D}$  is the appropriate diffusion matrix compatible with (3.15). In addition as  $\dot{S}_g = -\dot{S}_l = K \alpha_l (c_g - c_{sat})^+ / \rho_l$ , we may use the redundant equation (3.11):

$$\nabla \cdot \left( \frac{\alpha_g}{\rho_g} \mathbf{u}_g + \frac{\alpha_l}{\rho_l} \mathbf{u}_l \right) = \dot{S}_g \left( \frac{1}{\rho_g} - \frac{1}{\rho_l} \right). \quad (3.29)$$

### 3.3.2 Semi-discrete schemes

Let  $T$  be the final time and  $\delta t$  a time step. We denote by  $\phi^m$ ,  $m = 0, 1, \dots, N := T/\delta t$  the numerical solution of any physical quantity  $\phi$  at time  $m\delta t$ . Convection terms are approximated in time by the method of characteristics. Let  $X_j^m(x) \approx x - \mathbf{u}_j^m(x)\delta t$ . Then

$$(\partial_t \alpha_j + \mathbf{u}_j \cdot \nabla \alpha_j)|_{x, t=t^{m+1}} \approx \frac{1}{\delta t} (\alpha_j^{m+1}(x) - \alpha^m(X_j^m(x))).$$

Consider the following scheme

$$\frac{1}{\delta t} (\alpha_l^{m+1} - \alpha_l^m \circ X_l^m) + \alpha_l^{m+1} \left( \nabla \cdot \mathbf{u}_l^m + \frac{1}{\rho_l} K (c_g^m - c_{sat})^+ \right) = 0, \quad (3.30)$$

$$r_l^{m+1} = \alpha_l^{m+1} / \rho_l, \quad r_g^{m+1} = 1 - r_l^{m+1}, \quad \alpha_g^{m+1} = \rho_g r_g^{m+1} \quad (3.31)$$

$$\frac{1}{\delta t} \alpha_j^{m+1} (\mathbf{u}_j^{m+1} - \mathbf{u}_j^m \circ X_j^m) + \rho_j^{-1} \alpha_j^{m+1} \nabla p^{m+1} - \nu_j \nabla \cdot (\alpha_j^{m+1} \mathbf{D}(\mathbf{u}_j^{m+1})) \quad (3.32)$$

$$+ \gamma_j \rho_g^{-1} C_D \alpha_g^{m+1} |\mathbf{u}_g^{m+1} - \mathbf{u}_l^{m+1}| (\mathbf{u}_g^{m+1} - \mathbf{u}_l^{m+1}) = 0, \quad j = g, l,$$

$$\nabla \cdot (\rho_g^{-1} \alpha_g^{m+1} \mathbf{u}_g^{m+1} + \rho_l^{-1} \alpha_l^{m+1} \mathbf{u}_l^{m+1}) = \rho_l^{-1} K \alpha_l^{m+1} (c_g^{m+1} - c_{sat})^+ (\rho_g^{-1} - \rho_l^{-1}), \quad (3.33)$$

$$\frac{1}{\delta t} \alpha_l^{m+1} (C^{m+1} - C^m \circ X_j^m) - \nabla \cdot (\alpha_l^{m+1} \mathbf{D} \cdot \nabla C^{m+1}) + (0, 0, M_g K \alpha_l^m (c_g^m - c_{sat})^+)^T = 0, \quad (3.34)$$

For electroless plating the domain is  $\Omega^m = \{(x, y) : 0 < y < y^m(x), x \in (0, L)\}$ , so it is updated by

$$y^{m+1}(x) = y^m(x) + \delta t u_{g2}^{m+1}(x), \quad x \in (0, L)$$

**Remark 3.3.1** Because of the asymmetrical treatment of  $\alpha_g$  and  $\alpha_l$  the scheme (3.30) does *not* imply that

$$\frac{1}{\delta t} (\alpha_g^{m+1} - \alpha_g^m \circ X_g^m) + \alpha_g^{m+1} \nabla \cdot \mathbf{u}_g^m = \rho_l^{-1} \alpha_l^{m+1} K (c_g^m - c_{sat})^+. \quad (3.35)$$

However, by (3.30), (3.31), (3.33), we have

$$\begin{aligned} & \frac{1}{\delta t} (\alpha_g^{m+1} - \alpha_g^m \circ X_g^m) + \alpha_g^{m+1} \nabla \cdot \mathbf{u}_g^m + \frac{\rho_g}{\rho_l} (\alpha_l^{m+1} - \alpha_l^m) \nabla \cdot (\mathbf{u}_l^m - \mathbf{u}_g^m) \\ & + \frac{1}{\delta t} (\alpha_g^m \circ X_g^m - \alpha_g^m \circ X_l^m) + (\mathbf{u}_g^m - \mathbf{u}_l^m) \cdot \nabla \alpha_g^m \\ & = \rho_l^{-1} \alpha_l^{m+1} K (c_g^m - c_{sat})^+ + \rho_l^{-1} \left( \frac{\rho_g}{\rho_l} - 1 \right) (\alpha_l^{m+1} - \alpha_l^m) K (c_g^m - c_{sat})^+. \end{aligned} \quad (3.36)$$

By a Taylor expansion at  $x$ , we obtain

$$\alpha_g^m(X_l^m(x)) - \alpha_g^m(X_g^m(x)) = \delta t (\mathbf{u}_g^m - \mathbf{u}_l^m) \cdot \nabla \alpha_g^m(x) + O(\delta t^2), \quad (3.37)$$

and

$$\alpha_l^{m+1} - \alpha_l^m = -\delta t(\mathbf{u}_l \cdot \nabla \alpha_l^m + \alpha_l^{m+1} \nabla \cdot \mathbf{u}_l^m) - \delta t K \alpha_l^{m+1} (c_g^m - c_{sat})^+ + O(\delta t^2). \quad (3.38)$$

Plugging (3.37) and (3.38) into (3.36), we have

$$\frac{1}{\delta t}(\alpha_g^{m+1} - \alpha_g^m \circ X_g^m) + \alpha_g^{m+1} \nabla \cdot \mathbf{u}_g^m = \rho_l^{-1} \alpha_l^{m+1} K (c_g^m - c_{sat})^+ + O(\delta t). \quad (3.39)$$

So the scheme is consistent with the equation for  $\alpha_g$ .

### 3.3.3 Positivity

Positivity of  $\alpha_l^{m+1}$  holds only if  $\delta t$  is small enough. When positivity is required absolutely, an  $O(\delta t)$  modification of (3.30) forces the positivity of  $\alpha_l$ :

$$\begin{aligned} \frac{1}{\delta t} (\alpha_l^{m+1}(x) - \alpha_l^m(X_l^m(x))) + \alpha_l^{m+1} \left( \nabla \cdot \mathbf{u}_l^m + \frac{1}{\rho_l} K (c_g^m - c_{sat})^+ \right)^+ \\ = \alpha_l^m \left( \nabla \cdot \mathbf{u}_l^m + \frac{1}{\rho_l} K (c_g^m - c_{sat})^+ \right)^-. \end{aligned} \quad (3.40)$$

Indeed assume that  $\alpha_l^m$  is strictly positive, or more precisely that  $\alpha_l^m \geq \epsilon > 0$  for all  $x$ ; then we have

$$\begin{aligned} \alpha_l^{m+1} \left[ 1 + \delta t (\nabla \cdot \mathbf{u}_l^m + \frac{1}{\rho_l} K (c_g^m - c_{sat})^+)^+ \right] &= \alpha_l^m (X_l^m) + \delta t \alpha_l^m \left[ \nabla \cdot \mathbf{u}_l^m + \frac{1}{\rho_l} K (c_g^m - c_{sat})^+ \right]^- \\ &\geq \epsilon (1 + \delta t (\nabla \cdot \mathbf{u}_l^m + \frac{1}{\rho_l} K (c_g^m - c_{sat})^+)^-). \end{aligned} \quad (3.41)$$

1. Let us show first that (3.30) generates a bounded sequence  $\{\alpha_l^m\}_{m=1..N}$ . For clarity we assume homogeneous data at the boundaries. With simplified notations

$$\frac{1}{\delta t}(\alpha^{m+1} - \alpha^m \circ X^m) + \alpha^{m+1} (\nabla \cdot \mathbf{u}^m + \phi^m) = 0$$

A multiplication by  $\alpha^{m+1}$  and an integration on  $\Omega^{m+1}$  leads to

$$\|\alpha^{m+1}\|_{L^2}^2 = \int_{\Omega^{m+1}} [\alpha^{m+1} (\alpha^m \circ X^m - \delta t (\alpha^{m+1} \nabla \cdot \mathbf{u}^m + \phi^m))] dx$$

By the Cauchy-Schwarz inequality and the positivity of  $\phi^m$ ,

$$\|\alpha^{m+1}\|_{L^2}^2 \leq \|\alpha^{m+1}\|_{L^2} \left( \int_{\Omega^{m+1}} [\alpha^m \circ X^m - \delta t \alpha^{m+1} \nabla \cdot \mathbf{u}^m]^2 dx \right)^{\frac{1}{2}}.$$

The inverse of the determinant of the Jacobian of the transformation  $x \mapsto X^m(x)$  is  $1 + \delta t \nabla \cdot \mathbf{u} + O(\delta t^2)$ ; therefore, for any smooth function  $f$ , in particular with  $f = \alpha^m \circ X^m - \delta t \alpha^{m+1} \nabla \cdot \mathbf{u}^m = \alpha^m \circ X^m (1 - \delta t \nabla \cdot \mathbf{u}^m \circ X^m + O(\delta t^2))$ ,

$$\begin{aligned} \int_{\Omega^{m+1}} f^m \circ X^m &= \int_{\Omega^m} f^m (1 + \delta t \nabla \cdot \mathbf{u} + O(\delta t^2)) dx \\ \Rightarrow \|\alpha^{m+1}\|_{L^2} &\leq \|\alpha^m\|_{L^2} (1 + C(\|\nabla^2 \mathbf{u}^m\|_{L^\infty}) \delta t^2). \end{aligned}$$

where  $C()$  is a generic constant bounded by the Hessian of  $u$ . Thus  $\{\alpha_l^m\}_{m=1..N}$  is bounded.

2. Stability of the scheme for  $C$  is shown by the same argument.
3. Stability of the scheme for  $\mathbf{u}_g$  and  $\mathbf{u}_l$  is a consequence of a similar argument combined with the Ladhzyenskaya-Babuska-Brezzi saddle point theory (LBB) [47].

We denote by  $(\cdot, \cdot)$  the  $L^2$  inner product. For tensor-valued functions such that  $\mathbf{f}, \mathbf{g} \in L^2(\Omega(t))^{mn}$ ,  $m, n \in \mathbb{N}^+$ ,  $(\mathbf{f}, \mathbf{g}) = \sum_{i=1}^m \sum_{j=1}^n (f_{ij}, g_{ij})$ . With self explanatory notations, the equations for the velocities (3.32), (3.33) are written in variational form as:

Find  $\mathbf{u}_g, \mathbf{u}_l$  and  $p$  satisfying the Dirichlet conditions and such that,  $\forall \widehat{\mathbf{v}}_g, \widehat{\mathbf{v}}_l \in \mathbf{V}_0^{m+1} := (H_0^1(\Omega^{m+1}))^2$  and  $\forall \widehat{q} \in P^{m+1} := L^2(\Omega^{m+1})/\mathbb{R}$ ,

$$\begin{aligned} & (\beta_g \mathbf{u}_g, \widehat{\mathbf{v}}_g) + (\beta_l \mathbf{u}_l, \widehat{\mathbf{v}}_l) + \frac{1}{2} (\alpha_g D(\mathbf{u}_g), D(\widehat{\mathbf{v}}_g)) + \frac{1}{2} (\alpha_l D(\mathbf{u}_l), D(\widehat{\mathbf{v}}_l)) \\ & - \left( p, \nabla \cdot \left( \frac{\alpha_g}{\rho_g} \widehat{\mathbf{v}}_g + \frac{\alpha_l}{\rho_l} \widehat{\mathbf{v}}_l \right) \right) + \left( \widehat{q}, \nabla \cdot \left( \frac{\alpha_g}{\rho_g} \mathbf{u}_g + \frac{\alpha_l}{\rho_l} \mathbf{u}_l \right) \right) = (\mathbf{L}_g, \widehat{\mathbf{v}}_g) + (\mathbf{L}_l, \widehat{\mathbf{v}}_l) + (\widehat{q}, f). \end{aligned} \quad (3.42)$$

where, for  $j = g, l$ ,  $\alpha_j := \alpha_j^{m+1}$ ,  $\beta_j := \frac{1}{\delta t} \alpha_j + \frac{C_D}{\rho_g} \alpha_g |\mathbf{u}_g^m - \mathbf{u}_l^m|$ ,

$$\mathbf{L}_j := \frac{1}{\delta t} \alpha_j \mathbf{u}_l^m \circ X_j^m + \frac{C_D}{\rho_g} \alpha_g |\mathbf{u}_g^m - \mathbf{u}_l^m| \mathbf{u}_j^m, \quad f := \rho_l^{-1} K \alpha_l (c_g^{m+1} - c_{sat})^+ (\rho_g^{-1} - \rho_l^{-1}). \quad (3.43)$$

and where  $!g = l$ ,  $!l = g$ .

Note that the above is a semi-linearization of (3.32), (3.33). However in algorithm 1 below, the nonlinear problem is solved by an iterative fixed point which uses (3.42)-(3.43).

The LBB theorem says that the solution of (3.42) exists and is unique because, for every  $p \in P^{m+1}$  there is a (non-unique)  $\mathbf{w} \in \mathbf{V}_0^{m+1}$  with

$$(\nabla \cdot \mathbf{w}, \widehat{q}) = (f, \widehat{q}), \quad \forall \widehat{q} \in P^{m+1},$$

provided that  $\int_{\Gamma_{in}} \mathbf{u}_{in} \cdot \mathbf{n} = \int_{\Omega^{m+1}} f dx$ . Let us show stability in the special case  $f = 0$  because one can always subtract  $\mathbf{w}$  from  $\frac{\alpha_g}{\rho_g} \mathbf{u}_g + \frac{\alpha_l}{\rho_l} \mathbf{u}_l$  so as to work with  $\mathbf{u}_{g,in} = \mathbf{u}_{l,in} = 0$  and  $f = 0$ .

Thus, setting  $\widehat{\mathbf{v}}_g = \mathbf{u}_g$ ,  $\widehat{\mathbf{v}}_l = \mathbf{u}_l$  and  $\widehat{q} = p$  leads to

$$\frac{1}{\delta t} \|\sqrt{\alpha_g} \mathbf{u}_g\|_{L^2}^2 + \frac{1}{2} \|\sqrt{\alpha_g} D(\mathbf{u}_g)\|_{L^2}^2 + \frac{1}{\delta t} \|\sqrt{\alpha_l} \mathbf{u}_l\|_{L^2}^2 + \frac{1}{2} \|\sqrt{\alpha_l} D(\mathbf{u}_l)\|_{L^2}^2 \leq (\mathbf{L}_g, \mathbf{u}_g) + (\mathbf{L}_l, \mathbf{u}_l). \quad (3.44)$$

By the same argument used above, it implies that  $\mathbf{u}_j$ ,  $j = g, l$  is bounded. Indeed, assuming  $\alpha^m \geq 0$ ,

$$\begin{aligned} \delta t (\mathbf{L}_j, \mathbf{u}_j) &= \int_{\Omega^{m+1}} \alpha_j \mathbf{u}_j^m \circ X_j^m \cdot \mathbf{u}_j dx \leq \|\sqrt{\alpha_j} \mathbf{u}_j\|_{L^2} \left( \int_{\Omega^{m+1}} \alpha_j |\mathbf{u}_j^m \circ X_j^m|^2 dx \right)^{\frac{1}{2}} \\ &= \|\sqrt{\alpha_j} \mathbf{u}_j\|_{L^2} \left( \int_{\Omega^{m+1}} \left( \alpha_j^m \circ X_j^m - \alpha \delta t (\nabla \cdot \mathbf{u}_l^m + \frac{1}{\rho_l} K (c_g^m - c_{sat})^+) \right) |\mathbf{u}_j^m \circ X_j^m|^2 dx \right)^{\frac{1}{2}} \\ &\leq \|\sqrt{\alpha_j} \mathbf{u}_j\|_{L^2} \left( \int_{\Omega^{m+1}} (\alpha_j^m \circ X_j^m - \alpha \delta t \nabla \cdot \mathbf{u}_l^m) |\mathbf{u}_j^m \circ X_j^m|^2 dx \right)^{\frac{1}{2}} \end{aligned}$$

$$\begin{aligned}
&\leq \|\sqrt{\alpha_j} \mathbf{u}_j\|_{L^2} \left( \int_{\Omega^{m+1}} \alpha_j^m \circ X_j^m (1 - \delta t \nabla \cdot \mathbf{u}_l^m + O(\delta t^2)) |\mathbf{u}_j^m \circ X_j^m|^2 dx \right)^{\frac{1}{2}} \\
&= \|\sqrt{\alpha_j} \mathbf{u}_j\|_{L^2} \left( \int_{\Omega^m} (\alpha_j^m (1 + O(\delta t^2))) |\mathbf{u}_j^m|^2 dx \right)^{\frac{1}{2}} \\
&\leq \|\sqrt{\alpha_j} \mathbf{u}_j\|_{L^2} (1 + \delta t^2 C (\|c_g^m\|_{L^\infty}, \|\nabla^2 \mathbf{u}_l^m\|_{L^\infty})) \left\| \sqrt{\alpha_j^m} \mathbf{u}_j^m \right\|_{L^2}
\end{aligned} \tag{3.45}$$

for some generic constant  $C$  depending on  $\|c_g^m\|_{L^\infty}$  and  $\|\nabla^2 \mathbf{u}_l^m\|_{L^\infty}$ . Finally, we obtain

$$\| \mathbf{u}_g^{m+1}, \mathbf{u}_l^{m+1} \|_{m+1} \leq (1 + C \delta t^2) \| \mathbf{u}_g^m, \mathbf{u}_l^m \|_m + \delta t \frac{C_D}{\rho_g} \left\| \frac{\alpha_g}{\alpha_j^m} (\mathbf{u}_g^m - \mathbf{u}_l^m) \right\|_{L^\infty} \| \mathbf{u}_g^m, \mathbf{u}_l^m \|_m, \tag{3.46}$$

where

$$\| \mathbf{u}_g, \mathbf{u}_l \|_m^2 := \sum_{j=g,l} \left\| \sqrt{\alpha_{j,h}^m} \mathbf{u}_j \right\|_{L^2}^2 + \frac{1}{2} \delta t \left\| \sqrt{\alpha_{l,h}^m} D(\mathbf{u}_j) \right\|_{L^2}^2, \quad m = 0, \dots, N.$$

This estimate is optimal, but for the constant  $C$  which is the drawback of the characteristic method and for the  $L^\infty$  norm which is consequence of the unsophisticated treatment of the nonlinearity. Nevertheless, would these two be bounded, the scheme would be  $H^1$  stable.

4. Note that we have swept under the rug the fact that at level  $m$  the domain of definition of the functions is  $\Omega^m$  and at level  $m+1$  it is  $\Omega^{m+1}$ . The problem can be solved but at the cost of difficult notations and iterations between  $y^{m+1}$  and  $\mathbf{u}^{m+1}$ ; for details see [55].

## 3.4 Finite element implementation

For simplicity, the physical domain  $\Omega(t)$  is assumed to be a two-dimensional polygonal domain.

### 3.4.1 Mesh

Let  $\{\mathcal{K}_h(t)\}_{h>0}$  be an affine, shape regular (in the sense of Ciarlet[28]) family of mesh conforming to  $\Omega(t)$ . The conforming Lagrange finite element space of degree  $p$  on  $\Omega(t)$  is

$$X_{h,t}^p = \{v \in C^0(\Omega(t)) : v|_K \in P^p, \forall K \in \mathcal{K}_h(t)\}, \tag{3.47}$$

where  $P^p$  is the space of polynomials of degree  $p$  of  $\mathbb{R}^2$ .

Let  $\{\phi_1, \dots, \phi_{N_q}\}$  be the nodal Lagrange basis of  $X_{h,t}^1$ . If the vertices are denoted by  $\{\mathbf{q}^i\}_1^{N_q}$ , then  $\phi_i(\mathbf{q}_j) = \delta_{ij}$ . Let  $S_i$  be the support of  $\phi_i$  and let  $S_{ij} := S_i \cap S_j$ . If  $E$  is a union of triangles, define  $\mathcal{I}(E) := \{i \in \{1, \dots, N_q\} : |S_i \cap E| \neq 0\}$ . Finally, the local minimum mesh size of  $K \in \mathcal{K}_h(t)$  is  $h_K(t) := 1/\max_{i \in \mathcal{I}(K)} \|\nabla \phi_i\|_{L^\infty(K)}$ , and the global minimum mesh size is  $h(t) := \min_{K \in \mathcal{K}_h} h_K(t)$ .

We assume that the connectivity of the mesh  $\mathcal{K}_h(t)$  never changes with time.

### 3.4.2 Spatial discretization

We use the Hood-Taylor element: the velocities are in  $\mathbf{V}_h(t) := (X_{h,t}^2)^2$  and the pressure is in  $P_h(t) := X_{h,t}^1$ . For the volume fractions and the concentrations we use also  $P_h(t)$ .

Recall that the nodes of  $X_{h,t}^2$  are the vertices and the middle of the edges. Denote by  $\{\psi_1, \dots, \psi_{N_a}\}$  the nodal Lagrange basis of associated with the nodes  $\{\mathbf{a}_1, \dots, \mathbf{a}_{N_a}\}$  for  $X_{h,t}^2$ . For convenience, we define  $\Omega^m := \Omega(t^m)$ ,  $P_h^m = X_{h,t^m}^1$  and  $\mathbf{V}_h^m = (X_{h,t^m}^2)^2$ .

On the boundaries where Dirichlet conditions are set, the functions are known. We denote  $P_{0h}^m$  and  $\mathbf{V}_{0h}^m$ , the corresponding spaces where basis functions attached to a Dirichlet node are removed.

### Volume fractions

Given  $\alpha_{l,h}^m, c_{g,h}^m \in P_h^m$  and  $\mathbf{u}_{l,h}^m \in \mathbf{V}_h^m$ , find  $\alpha_{l,h}^{m+1} \in P_h^{m+1}$  satisfying the Dirichlet boundary conditions and such that

$$\frac{1}{\delta t} \left( \alpha_{l,h}^{m+1} - \alpha_{l,h}^m \circ X_{l,h}^m, \widehat{q}_h \right) + \left( \alpha_{l,h}^{m+1} (\nabla \cdot \mathbf{u}_{l,h}^m + \rho_l^{-1} K(c_{g,h}^m - c_{sat})^+), \widehat{q}_h \right) = 0, \quad \forall \widehat{q}_h \in P_{0h}^{m+1}, \quad (3.48)$$

where  $X_{j,h}^m(x) = x - \delta t \mathbf{u}_{j,h}^m(x)$  for  $x \in \Omega^m$ ,  $j = g, l$ . Then we let  $\alpha_{g,h}^{m+1} = \rho_g(1 - \rho_l^{-1} \alpha_{l,h}^{m+1})$ .

**Remark 3.4.1** A modification similar to (3.40) will insure the positivity of  $\alpha_{l,h}^{m+1}$ .

### Concentration profiles

Given  $\alpha_{l,h}^{m+1} \in P_h^{m+1}$ ,  $\alpha_{l,h}^m \in P_h^m$ ,  $\mathbf{u}_{l,h}^m \in \mathbf{V}_h^m$ ,  $C_h^m \in (P_h^{m+1})^{2+k_M}$ , find  $C_h^{m+1} \in (P_h^{m+1})^{2+k_M}$  such that

$$\begin{aligned} \frac{1}{\delta t} \left( \alpha_{l,h}^{m+1} (C_h^{m+1} - C_h^m \circ X_l^m), \widehat{w}_h \right) + \left( \alpha_{l,h}^{m+1} \mathbf{D} \nabla C_h^{m+1}, \nabla \widehat{w}_h \right) + \left( M_g K \alpha_{l,h}^m (c_{g,h}^m - c_{sat})^+, \widehat{w}_{g,h} \right) \\ + \left( I(E_{mix,h}^{m+1}) (C_h^{m+1})^\kappa, \widehat{w}_h \right)_{L^2(S(t^{m+1}))} = 0 \quad \forall \widehat{w}_h \in (P_{0h}^{m+1})^{2+k_M}, \end{aligned} \quad (3.49)$$

subject to

$$\sum_{j=s,k} i_j(E_{mix,h}^{m+1}) (c_{j,h}^{m+1})^{\kappa_j}(\mathbf{q}_i) = 0, \quad \text{for each nodal point } \mathbf{q}_i \text{ on } S^m \quad (3.50)$$

where  $\widehat{w}_{g,h}$  is the last component of  $\widehat{w}_h$  and

$$\begin{aligned} I(E_{mix,h}^{m+1}) = \text{diag} \left( \frac{|i_s(E_{mix,h}^{m+1})|}{z_s F}, \frac{|i_k(E_{mix,h}^{m+1})|}{z_k F}, -\frac{\beta |i_s(E_{mix,h}^{m+1})|}{z_s F} \right), \\ (C_h^{m+1})^\kappa = \left( (c_{s,h}^{m+1})^{\kappa_s}, (c_{k,h}^{m+1})^{\kappa_k}, (c_{s,h}^{m+1})^{\kappa_s} \right)^T \end{aligned}$$

for  $i_s, i_k$  defined by (3.20).

### Two phase flow

Given  $\alpha_{j,h}^{m+1} \in P_h^{m+1}$ ,  $j = g, l$ ,  $c_{g,h}^{m+1} \in P_h^{m+1}$ , and  $\mathbf{u}_{j,h}^m \in \mathbf{V}_h^m$ , find  $\mathbf{u}_{j,h}^{m+1} \in \mathbf{V}_h^{m+1}$ ,  $j = g, l$  and  $p_h^{m+1} \in P_h^{m+1}/\mathbb{R}$  such that

$$\begin{aligned} \sum_{j=g,l} \left\{ \frac{1}{\delta t} \left( \alpha_{j,h}^{m+1} (\mathbf{u}_{j,h}^{m+1} - \mathbf{u}_j^m \circ X_{j,h}^m), \widehat{\mathbf{v}}_{j,h} \right) + \frac{1}{2} \nu_j \left( \alpha_j^{m+1} D(\mathbf{u}_{j,h}^{m+1}), D(\mathbf{v}_{j,h}) \right) \right. \\ \left. + \gamma_j \rho_g^{-1} C_D \left( \alpha_{g,h}^{m+1} |\mathbf{u}_{g,h}^{m+1} - \mathbf{u}_{l,h}^{m+1}| (\mathbf{u}_{g,h}^{m+1} - \mathbf{u}_{l,h}^{m+1}), \widehat{\mathbf{v}}_{j,h} \right) - (p_h^{m+1}, \nabla \cdot (\rho_j^{-1} \alpha_{j,h}^{m+1} \widehat{\mathbf{v}}_{j,h})) \right\} = 0 \end{aligned} \quad (3.51)$$



$$\left( \widehat{q}_h, \nabla \cdot (\rho_g^{-1} \alpha_{g,h}^{m+1} \mathbf{u}_{g,h}^{m+1} + \rho_l^{-1} \alpha_{l,h}^{m+1} \mathbf{u}_{l,h}^{m+1}) \right) = \left( \widehat{q}_h, \frac{K}{\rho_l} \alpha_{l,h}^{m+1} (c_{g,h}^{m+1} - c_{sat})^+ (\rho_g^{-1} - \rho_l^{-1}) \right) \quad (3.52)$$

for all  $\widehat{\mathbf{v}}_{j,h} \in \mathbf{V}_{0h}^{m+1}$ ,  $j = g, l$  and  $\widehat{q}_h \in P_h^{m+1}/\mathbb{R}$ .

### 3.4.3 Fixed point iterative solution of (3.51), (3.52)

The system (3.51)-(3.52) is nonlinear. An iterative algorithm is described in Algorithm 1.

---

**Algorithm 1 :** A semi-lineariazation for solving (3.51)-(3.52).

---

```

1 Let  $\mathbf{L}_g, \mathbf{L}_l, f$  be defined by (3.43).
   Data : Set  $\mathbf{u}_j = \mathbf{u}_{j,h}^m$ ,  $j = g, l$ .
2 for  $n = 1 \dots N$  do
3   Set  $\beta_j = \left( \frac{1}{\delta t} \alpha_{j,h}^{m+1} + \frac{C_D}{\rho_g} \alpha_{g,h}^{m+1} |\mathbf{u}_g - \mathbf{u}_l| \right)$ ,
4   Find  $\mathbf{u}_g, \mathbf{u}_l$  and  $p$  satisfying the Dirichlet conditions and such that,  $\forall \widehat{\mathbf{v}}_g, \widehat{\mathbf{v}}_l \in \mathbf{V}_{0h}^{m+1}$  and
       $\forall \widehat{q} \in P_h^{m+1}/\mathbb{R}$ 
      
$$\begin{aligned} & (\beta_g \mathbf{u}_g, \widehat{\mathbf{v}}_g) + (\beta_l \mathbf{u}_l, \widehat{\mathbf{v}}_l) + \frac{1}{2} (\alpha_{g,h}^{m+1} D(\mathbf{u}_g), D(\widehat{\mathbf{v}}_g)) + \frac{1}{2} (\alpha_{l,h}^{m+1} D(\mathbf{u}_l), D(\widehat{\mathbf{v}}_l)) \\ & - \left( p, \nabla \cdot \left( \frac{\alpha_{g,h}^{m+1}}{\rho_g} \widehat{\mathbf{v}}_g + \frac{\alpha_{l,h}^{m+1}}{\rho_l} \widehat{\mathbf{v}}_l \right) \right) + \left( \widehat{q}, \nabla \cdot \left( \frac{\alpha_{g,h}^{m+1}}{\rho_g} \mathbf{u}_g + \frac{\alpha_{l,h}^{m+1}}{\rho_l} \mathbf{u}_l \right) \right) \\ & = (\mathbf{L}_g, \widehat{\mathbf{v}}_g) + (\mathbf{L}_l, \widehat{\mathbf{v}}_l) + (\widehat{q}, f). \end{aligned} \quad (3.53)$$

5 end
6 Set  $\mathbf{u}_j^{n+1} = \mathbf{u}_j$ ,  $j = g, l$ .
```

---

### 3.4.4 Consistence and stability

Variational formulations discretized by finite element methods inherit the stability and consistency of the continuous equations. The LBB theorem applies also to the Hood-Taylor element for velocity pressure problems. Therefore, as in the continuous case, the  $H^1$  norms of  $\alpha_j^{m+1}, \mathbf{u}_j^{m+1}, C_j^{m+1}$  are less than  $(1 + C(\|\nabla^2 \mathbf{u}_l^m\|_{L^\infty}) \delta t)$  times the  $H^1$  norms of  $\alpha_j^m, \mathbf{u}_j^m, C_j^m$ . If we could show that  $C(\cdot)$  is bounded, then it would imply that the scheme converges when  $\delta t \rightarrow 0$ .

### 3.4.5 Solvability of the linear system in matrix form

Let  $\boldsymbol{\zeta} = (\boldsymbol{\zeta}_g, \boldsymbol{\zeta}_l) \in (\mathbf{V}_h^{m+1})^2$ ,  $\alpha_{j,h}^{m+1} \in P_h^{m+1}$ ,  $\alpha_{j,h} \geq \epsilon$  for some constant  $\epsilon > 0$ ,  $j = g, l$ .

To study the solvability of (3.51)-(3.52), we consider a simpler case with  $\mathbf{u}_g = \mathbf{u}_l = 0$  on  $\partial\Omega^{m+1} \setminus \Gamma_{out}$ , and take the linearized approximation on the drag force terms. The problem reads: Find  $\mathbf{u}_h^{m+1} := (\mathbf{u}_{g,h}^{m+1}, \mathbf{u}_{l,h}^{m+1}) \in (\mathbf{V}_{0h}^{m+1})^2$  and  $p_h^{m+1} \in P_h^{m+1}/\mathbb{R}$  satisfying

$$a_{\boldsymbol{\zeta}}(\mathbf{u}_h^{m+1}, \widehat{\mathbf{v}}_h) + b(p_h^{m+1}, \widehat{\mathbf{v}}_h) = F(\widehat{\mathbf{v}}_h), \quad b(\widehat{q}_h, \mathbf{u}_h^{m+1}) = G(\widehat{q}_h), \quad (3.54)$$

where, for  $\mathbf{u} = (\mathbf{u}_g, \mathbf{u}_l), \mathbf{v} = (\mathbf{v}_g, \mathbf{v}_l) \in (\mathbf{V}_{0h}^{m+1})^2, q \in P_h^{m+1},$

$$\begin{aligned} a_\zeta(\mathbf{u}, \mathbf{v}) &= \sum_{j=g,l} \left[ \frac{1}{\delta t} \left( \alpha_{j,h}^{m+1} \mathbf{u}_j, \mathbf{v}_j \right) + \frac{1}{2} \nu_j \left( \alpha_{j,h}^{m+1} D(\mathbf{u}_j), D(\mathbf{v}_j) \right) \right] \\ &\quad + \rho_g^{-1} C_D \left( \alpha_{g,h}^{m+1} |\zeta_g - \zeta_l| (\mathbf{u}_g - \mathbf{u}_l), \mathbf{v}_g - \mathbf{v}_l \right) \\ b(q, \mathbf{v}) &= - \left( q, \nabla \cdot (\rho_g^{-1} \alpha_{g,h}^{m+1} \mathbf{v}_g + \rho_l^{-1} \alpha_{l,h}^{m+1} \mathbf{v}_l) \right) \\ F(\mathbf{v}) &= \sum_{j=l,g} \frac{1}{\delta t} \left( \alpha_{j,h}^{m+1} \mathbf{u}_{j,h}^m(X_{j,h}^m(x)), \mathbf{v}_j \right) \quad G(q) = \left( q, \rho_l^{-1} K \alpha_{l,h}^{m+1} (c_{g,h}^{m+1} - c_{sat})^+ (\rho_g^{-1} - \rho_l^{-1}) \right). \end{aligned} \quad (3.55)$$

On the basis of  $\mathbf{V}_h^{m+1}$  and  $P_h^{m+1}$ , we can write

$$\mathbf{u}_{g,h}^{m+1} = \sum_{i=1}^{2N_a} u_{g,i}^{m+1} \psi_i, \quad \mathbf{u}_{l,h}^{m+1} = \sum_{i=1}^{2N_a} u_{l,i}^{m+1} \psi_i, \quad p_h^{m+1} = \sum_{i=1}^{N_q} p_i^{m+1} \phi_i, \quad (3.56)$$

More precisely  $\{\psi_1, \dots, \psi_{2N_a}\}$  is  $\{\psi_1 \mathbf{e}_1, \dots, \psi_{N_a} \mathbf{e}_1, \psi_1 \mathbf{e}_2, \dots, \psi_{N_a} \mathbf{e}_2\}$  for  $\mathbf{e}_1 = (1, 0)^T$  and  $\mathbf{e}_2 = (0, 1)^T$ .

Problem (3.54) can be formally expressed as a system of linear equations:

$$\Phi \mathbf{U}^{m+1} = \mathbf{F}^m, \quad (3.57)$$

where  $\Phi$  is a  $(4N_a + N_q) \times (4N_a + N_q)$  matrix,  $\mathbf{U}^{m+1}$  and  $\mathbf{F}^m$  are  $(4N_a + N_q)$  vectors. Note that  $\Phi$  has the form

$$\Phi = \begin{pmatrix} A & B \\ B^T & O \end{pmatrix}, \quad \text{with } A = \begin{pmatrix} A_g & A_{mix} \\ A_{mix} & A_l \end{pmatrix}. \quad (3.58)$$

In the above,

$$\begin{aligned} A_k &= \left( \frac{1}{\delta t} \left( \alpha_{k,h}^{m+1} \psi_i, \psi_j \right) + \frac{1}{2} \nu_k \left( \alpha_{k,h}^{m+1} D(\psi_i), D(\psi_j) \right) + \rho_g^{-1} C_D \left( \alpha_{g,h}^{m+1} |\zeta_g - \zeta_l| \psi_i, \psi_j \right) \right)_{i,j=1,\dots,2N_a}, \quad k = g, l, \\ A_{mix} &= \left( -\rho_g^{-1} C_D \left( \alpha_{g,h}^{m+1} |\zeta_g - \zeta_l| \psi_i, \psi_j \right) \right)_{i,j=1,\dots,2N_a}, \\ B &= \begin{pmatrix} - \left( \phi_j, \nabla \cdot (\rho_g^{-1} \alpha_{g,h}^{m+1} \psi_i) \right) \\ - \left( \phi_j, \nabla \cdot (\rho_l^{-1} \alpha_{l,h}^{m+1} \psi_i) \right) \end{pmatrix}_{i=1,\dots,4N_a; j=1,\dots,N_q}. \end{aligned}$$

**Proposition 3.4.1** The linear system (3.57) is uniquely solvable.

*Proof.* According to the Ladyzhenskaya-Babuska-Brezzi theorem [47] the saddle point problem (3.53) is well posed when for  $p \in P_h^{m+1}/\mathbb{R}$ , there exists  $\mathbf{v} \in \mathbf{V}_{0h}^{m+1}$  such that

$$\frac{(p, \nabla \cdot \mathbf{v})}{\|\mathbf{v}\|_{H^1}} \geq c \|p\|_{L^2/\mathbb{R}} \quad \text{for some } c > 0. \quad (3.59)$$

Therefore  $\Phi$  has full rank and is non singular.

### 3.4.6 Iterative process

At each time step, (3.48), is solved first, then (3.49)-(3.50) is solved iteratively by using a semi-linearization of the nonlinear boundary terms. Then (3.51),(3.52) is solved iteratively by a semi-

linearization of the nonlinear terms; each block involves the solution of a well posed symmetric linear system. Finally  $S^m$  is updated by (3.23). Algorithm 2 summarises the procedure.

Note that the computational domain is  $\Omega^m = \{(x, y), 0 < x < L, 0 < y < y^m(x)\}$ .

---

**Algorithm 2 :** Algorithm for solving the full system of equations.

---

**Data :**  $\alpha_{g,h}^m, \alpha_{l,h}^m, \mathbf{u}_{g,h}^m, \mathbf{u}_{l,h}^m, p_h^m, c_{s,h}^m, c_{k,h}^m, c_{g,h}^m, E_{mix,h}^m$ , and  $y^m$

- 1 Set initial data  $\alpha_{g,h}^0, \alpha_{l,h}^0, \mathbf{u}_{g,h}^0, \mathbf{u}_{l,h}^0, c_{s,h}^0, c_{k,h}^0, c_{g,h}^0, E_{mix,h}^0$ ;
- 2 **for**  $m$  **do**
- 3     Solve (3.48) to get  $\alpha_{g,h}^{m+1}, \alpha_{l,h}^{m+1}$ ;
- 4     Initial guess:  $E_{mix,h}^{m+1,0} = E_{mix,h}^m, C_h^{m+1,0} = \text{solution to (3.49) when mixed potential is } E_{mix,h}^{m+1,0}$ ;
- 5     **while**  $\|C_h^{m+1,k+1} - C_h^{m+1,k}\| \geq \text{tolerance}$  **do**
- 6         Initial guess:  $E_{mix,h}^{m+1,k+1,0} = E_{mix,h}^{m+1,k}$ ;
- 7         **while**  $\|E_{mix,h}^{m+1,k+1,l+1} - E_{mix,h}^{m+1,k+1,l}\|_{L^2(S^m)} \geq \text{tolerance}$  **do**
- 8             Solve (3.49) to get  $c_{s,h}^{m+1,k+1,l+1}, c_{k,h}^{m+1,k+1,l+1}, c_{g,h}^{m+1,k+1,l+1}$ ;
- 9             Solve (3.50) to get  $E_{mix,h}^{m+1,k+1,l*}$ ;
- 10              $E_{mix,h}^{m+1,k+1,l+1} = \xi E_{mix,h}^{m+1,k+1,l*} + (1 - \xi) E_{mix,h}^{m+1,k+1,l}, 0 < \xi < 1$ ;
- 11         **end**
- 12     **end**
- 13     Solve (3.51)-(3.52) to get,  $\mathbf{u}_{g,h}^{m+1}, \mathbf{u}_{l,h}^{m+1}, p_h^{m+1}$  (Using Algorithm 1);
- 14     For the free boundary case change the mesh by  $y^{m+1} = y^m + \delta t u_{2,g,h}^{m+1}$ ;
- 15 **end**

---

## 3.5 Numerical simulation

### 3.5.1 One-dimensional electroless nickel plating problem

Here we reproduce, with a two dimensional computation, the one-dimensional study by Kim and Sohn [66]. In their work, the electroless nickel plating process on a rotating disk with constant angular velocity is considered. In this situation, the velocity field near the surface of the rotating disk can be approximated by a uniformly distributed flow towards the plating surface. In addition, the thickness of diffusion layer is assumed uniform on the surface. Consequently, for the modeling, the domain becomes one-dimensional. Given that the gas generation is not considered and only the steady state is computed in [66], a single phase recovery  $r_l = 1$ ,  $c_g = 0$  is applied. Finally, four partial reactions in the electroless nickel plating process are considered:



All chemical species are labeled as follows:  $c_1$  is the concentration of the anodic hypophosphite ( $\text{H}_2\text{PO}_2^-$ ),  $c_2$  the concentration of the cathodic hypophosphite,  $c_3$  the concentration of the nickel ion ( $\text{Ni}^{2+}$ ), and  $c_4$  the concentration of the hydrogen ion ( $\text{H}^+$ ). Now the two-dimensional analogue can be formulated: Let  $\Omega = (0, \delta_3) \times (0, \epsilon)$ , where  $\delta_3$  is the thickness of the diffusion layer

Table 3.1: Physical parameters used in the simulation by Kim and Sohn [66], which are valid for  $pH = 4.5$  and the concentration of  $H_2PO_2^- = 0.3$  M

	$H^+$	$Ni^{2+}$	$H_2PO_2^-$ (cathodic)	$H_2PO_2^-$ (anodic)
$i_0$ ( $A/cm^2$ )	$1.5 \times 10^{-4}$ <sup>a</sup>	$1.5 \times 10^{-7}$ <sup>b</sup>	$6.0 \times 10^{-4}$	$8.9 \times 10^{-3}$
$D$ ( $cm^2/s$ )	$4.5 \times 10^{-5}$ <sup>a</sup>	$0.5 \times 10^{-6}$ <sup>c</sup>	$1.7 \times 10^{-5}$	$1.7 \times 10^{-5}$
$\alpha$	0.79 <sup>a</sup>	0.79 <sup>c</sup>	0.2	0.9
$\beta$	0.21 <sup>a</sup>	0.21 <sup>c</sup>	0.8	0.1
$z$	1	2	1	4
$\gamma$	1.0 <sup>a</sup>	1.0 <sup>c</sup>	0.3	1.0
$E_0$ (V) <sup>d</sup>	-0.101	-0.147	-0.806	-0.878
$c_0$ (M)	$3.162 \times 10^{-5}$ <sup>e</sup>	0.1	0.3	0.3
subscript $j$	4	3	2	1

<sup>a</sup> Estimated from the literature [5]. <sup>b</sup> Assumed in this study. <sup>c</sup> Taken from the literature [56]. <sup>d</sup> Calculated based on the literature [31]. all values except  $E_{03}$  ( $Ni^{2+}$ ) depend on  $pH$  (see (3.66)). <sup>e</sup> If  $pH = x$ , then  $c_{04} = 10^{-x}$  (M).  $i_0$ : Exchange current density,  $D$ : Diffusion coefficient.  $\alpha$ : Anodic transfer coefficient,  $\beta$  Cathodic transfer coefficient.  $z$ : Number of electron transport,  $\gamma$ : Reaction order,  $E_0$ : Equilibrium potential ( $90^\circ C$ )  $c_0$  inlet and initial concentration

Table 3.2: Conditions assumed in [66] for performing our simulations

Experimental conditions	
Angular velocity $\omega$	400 rpm
Kinematic viscosity $\nu$	$1.2 \times 10^{-2}$ $cm^2/s$
Temperature $\theta$	90 $^\circ C$
Composition of electrolytes	
$NiSO_4$ (nickel sulfate)	0.1 M
$NaH_2PO_2$ (sodium hypophosphite)	0.3 M
$pH$	4.0 – 5.3

for nickel and  $\epsilon \ll \delta_3$  is a small positive number. The thickness of the diffusion layer for species  $j$  is given in [74]:

$$\delta_j = 1.61 D_j^{1/3} \omega^{-1/2} \nu^{1/6}. \quad (3.61)$$

The governing equation for the concentration profile is given by

$$\partial_t c_j + \mathbf{u} \cdot \nabla c_j - D_j \Delta c_j = 0 \quad \text{in } \Omega, \quad (3.62)$$

subject to the boundary conditions

$$\begin{aligned}
c_j &= c_{0j} \quad \text{at } x = \delta_3, \quad -D_j \frac{\partial c_j}{\partial n} = 0 \quad \text{at } y = 0, \epsilon, \\
-D_j \frac{\partial c_j}{\partial n} &= \frac{|i_1(E_{mix})|}{z_1 F} \left( \frac{(1-r)c_1}{c_{01}} \right)^{\gamma_1} + \frac{|i_2(E_{mix})|}{z_2 F} \left( \frac{rc_2}{c_{02}} \right)^{\gamma_2} \quad j = 1, 2, \\
-D_j \frac{\partial c_j}{\partial n} &= \frac{|i_j(E_{mix})|}{z_j F} \left( \frac{c_1}{c_{01}} \right)^{\gamma_j} \quad j = 3, 4 \quad \text{at } x = 0.
\end{aligned} \quad (3.63)$$

with the electron balance constraint

$$\sum_{j=1}^4 \frac{i_j(E_{mix})}{z_j F} \left( \frac{c_j}{c_{0j}} \right)^{\gamma_j} = 0. \quad (3.64)$$

The velocity field can be expressed as in [74]:

$$\mathbf{u} = (-ax^2\omega^{3/2}\nu^{-1/2}, 0)^T \quad (3.65)$$

where  $a = 0.51023$  is an experimental constant,  $r = 0.995$  is the ratio between the hypophosphite anodic part and the cathodic part on the reacting surface. The equilibrium potential  $E_{0j}$  for species  $j$  can be approximated by the Nernst equation, with  $pH = \log(c_{04})$ :

$$\begin{aligned} E_{01} &= -0.878 + \frac{0.25R\theta}{F} \log(10^{4.5}c_{04}), & E_{02} &= -0.806 + \frac{0.3R\theta}{F} \log(10^{4.5}c_{04}), \\ E_{03} &= -0.147, & E_{04} &= -0.101 + \frac{R\theta}{F} \log(10^{4.5}c_{04}). \end{aligned} \quad (3.66)$$

By simulating system (3.62), (3.63), and (3.64), with the physical constants given in Table 3.1,

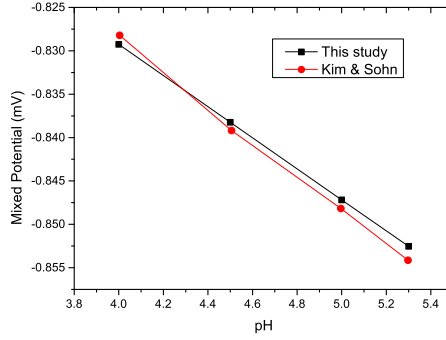


Figure 3.3: In red, the mixed potential  $E_{mix}$  computed by the one dimensional system (3.63) versus  $pH = \log c_{04}$ . In black, the same but computed with the full two dimensional system.

until a steady state is reached, the numerical tests show that the present model agrees well with the previous 1D studies of Kim and Sohn [66]: see Figures 3.3 and 3.4.

Regarding (3.60), atomic nickel and phosphorus are deposited on the surface during the electroless process. The deposition thickness can be estimated in terms of the current densities:

$$\left( \frac{i_2(E_{mix}) (c_2|_{x=0}/c_{02}) V_P}{z_2 F} + \frac{i_3(E_{mix}) (c_3|_{x=0}/c_{03}) V_{Ni}}{z_3 F} \right) t, \quad (3.67)$$

where  $V_P$ ,  $V_{Ni}$  are molar volumes of phosphorus and nickel, respectively, and  $t$  is the deposition time.

### 3.5.2 Two species in a gas-liquid two phase flow

Let the initial domain  $\Omega$  be a rectangular of size  $0.01 \times 0.001$  (in meters). We consider complexed (by tartrate, denoted by L) copper ions, formaldehyde, and hydrogen dissolved in water, which

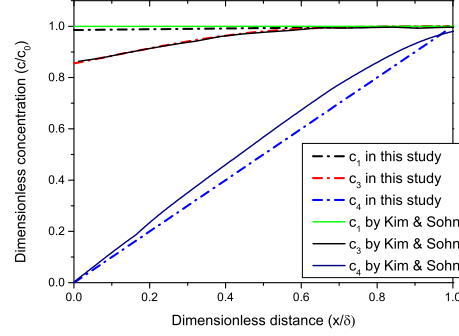
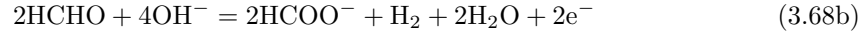
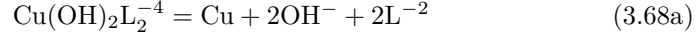


Figure 3.4: Concentration profiles of three chemical species versus  $x$  computed by the one dimensional system (3.63) and compared with the results of the full two dimensional system.

are denoted by the subscriptions  $s, k, g$ , respectively, for the chemical species transport equations.

The chemical reaction can be expressed as the following two partial reactions:



Given the above equations, we also use the subscriptions  $s$  and  $k$  to represent the quantities corresponding to (3.68a) and (3.68b), respectively.

The values of the physical constants are listed in Table 3.3.

physical quantity	value	physical quantity	value
$\rho_l$ ( $\text{kg}/\text{m}^3$ )	995.65	$\rho_g$ ( $\text{kg}/\text{m}^3$ )	1.161
$\rho_0$ ( $\text{kg}/\text{m}^3$ )	1.161	$\mu_g$ ( $\text{kg}/\text{m} \cdot \text{s}$ )	$1.86 \times 10^{-5}$
$\mu_l$ ( $\text{kg}/\text{m} \cdot \text{s}$ )	$7.977 \times 10^{-4}$	$d_0$ (m)	0.001
$u_0$ (m/s)	0.001	$c_{sat}$ ( $\text{mol}/\text{m}^3$ )	0
$i_g$ ( $\text{A}/\text{m}^2$ )	$1.0 \times 10^{-2}$	$i_s$ ( $\text{A}/\text{m}^2$ )	$1.0 \times 10^{-2}$
$i_k$ ( $\text{A}/\text{m}^2$ )	10	$R$ ( $\text{J}/\text{K} \cdot \text{mol}$ )	8.314
$K$ ( $\text{kg}/\text{mol} \cdot \text{s}$ )	$3.87 \times 10^{-4}$	$M_g$ ( $\text{mol}/\text{kg}$ )	500
$c_{g,0}$ ( $\text{mol}/\text{m}^3$ )	1	$c_{s,0}$ ( $\text{mol}/\text{m}^3$ )	39.34
$c_{k,0}$ ( $\text{mol}/\text{m}^3$ )	77.58	$D_g$ ( $\text{m}^2/\text{s}$ )	$2 \times 10^{-8}$
$D_s$ ( $\text{m}^2/\text{s}$ )	$7 \times 10^{-10}$	$D_k$ ( $\text{m}^2/\text{s}$ )	$1.2 \times 10^{-9}$
$z_s$ (1)	2	$z_k$ (1)	4
$\alpha_s$ (1)	0.67	$\alpha_k$ (1)	0.37
$\beta_s$ (1)	0.33	$\beta_k$ (1)	0.63
$\theta$ (K)	363.15	$E_s$ (V)	-0.266
$E_k$ (V)	1.5	$C_D$ (1)	242220
$\alpha$ (1)	0.0005		

Table 3.3: Parameters used in Section 3.5.2.

For convenience, the following scalings are applied:

$$\begin{aligned}
L &\rightarrow \frac{L}{d_0} \quad (L \text{ is any length}), \quad \rho_l \rightarrow \frac{\rho_l}{\rho_0}, \quad \rho_g \rightarrow \frac{\rho_g}{\rho_0}, \\
\mu_l &\rightarrow \frac{\mu_l}{\rho_0 d_0 u_0}, \quad \mu_g \rightarrow \frac{\mu_g}{\rho_0 d_0 u_0}, \quad c_g \rightarrow \frac{c_g}{c_{g0}}, \quad c_k \rightarrow \frac{c_k}{c_{k0}}, \quad c_s \rightarrow \frac{c_s}{c_{s0}}, \quad K \rightarrow \frac{d_0 c_{g0}}{\rho_0 u_0} K, \\
L_g &\rightarrow \frac{L_g}{u_0 c_{g0} z_s F}, \quad L_s \rightarrow \frac{L_s}{u_0 c_{s0} z_s F}, \quad L_k \rightarrow \frac{L_k}{u_0 c_{k0} z_k F}, \quad D_g \rightarrow \frac{D_g}{u_0 d_0}, \quad D_s \rightarrow \frac{D_s}{u_0 d_0}, \quad D_k \rightarrow \frac{D_k}{u_0 d_k}, \\
i_g &\rightarrow \frac{i_g}{u_0 c_{g0} z_s F}, \quad i_s \rightarrow \frac{i_s}{u_0 c_{s0} z_s F}, \quad i_k \rightarrow \frac{i_k}{u_0 c_{k0} z_k F}.
\end{aligned} \tag{3.69}$$

The initial conditions are set to: constant phase ratio and Poiseuille flow:

$$r_g^0 = \epsilon, \quad r_l^0 = 1 - \epsilon, \quad \mathbf{u}_g^0 = \mathbf{u}_l^0 = (0.69y(1-y), 0)^T, \tag{3.70}$$

with  $\epsilon = 0.0001$ . Also, let  $C^0 = (c_s^0, c_k^0, c_g^0)^T$  satisfies

$$-\nabla \cdot (r_l^0 \mathbf{D} \nabla C^0) = 0, \quad C^0|_{\Gamma_{in}} = (1, 1, 0)^T, \quad \frac{\partial C^0}{\partial n}|_{\Gamma_{out} \cup \Gamma_{wall}} = 0 \tag{3.71}$$

plus the first equation in (3.73) subject to (3.21). The inflow values are

$$\mathbf{u}_g^{m+1}|_{\Gamma_{in}} = \mathbf{u}_l^{m+1}|_{\Gamma_{in}} = (y(1-y), 0)^T, \quad c_g|_{\Gamma_{in}} = 0, \quad c_s|_{\Gamma_{in}} = c_k|_{\Gamma_{in}} = 1, \quad r_l|_{\Gamma_{in}} = 1 - \epsilon. \tag{3.72}$$

The boundary conditions on  $S(t^{m+1})$  are

$$-D_p \frac{\partial c_p^{m+1}}{\partial n} = \chi r_l^{m+1} |i_p^{m+1}| c_p^{m+1}, \quad p = s, g, k, \quad \mathbf{u}_g^{m+1} = \mathbf{u}_l^{m+1} = \alpha \chi r_l^{m+1} |i_s^{m+1}| c_s^{m+1}, \tag{3.73}$$

where  $\alpha = 0.0005$  and

$$\chi(x, y) = \begin{cases} x - \frac{3}{4} + \frac{1}{4} \sin(2\pi(x - \frac{1}{4})), & 1 \leq x < 1.5, \\ 1, & 1.5 \leq x < 5.5, \\ \frac{17}{4} - x - \frac{1}{4} \sin(2\pi(x - \frac{19}{4})), & 5.5 \leq x < 6, \\ 0, & 0 \leq x < 1 \text{ or } 6 \leq x \leq 10. \end{cases} \tag{3.74}$$

Boundary conditions on  $\Gamma_{out}$  and  $\Gamma_{wall}$  are as in Section 3.2.4. See also Figure 3.1.

**Remark 3.5.1** We note that  $\alpha = 0.0005$  is much larger than the experimental values; the numerical simulations produce  $u_{g2}$  (and  $u_{l2}$ ) of magnitude in the order  $O(10^{-4})$ . On the other hand, the deposition rate in a typical experiment is of order  $1 \mu m$  per hours [128], which is not larger than  $O(10^{-6})$ . Yet the numerical test is conducted to validate the numerical method when the evolution of the domain is larger than real life values.

### Convergence

First, we conduct the convergence test for different time step with a fixed mesh. To obtain a “reference solution”, the system (3.48)-(3.52) is solved with a  $50 \times 10$  uniform mesh and a small time step  $\delta t = 0.01$  and  $T = 10$ . The convergence with respect to  $\delta t$  is studied without changing the mesh; results are given in Table 3.4 and the rate of convergence for each variable is presented in Figure 3.5. Numerical tests for solving two phase flow problem and volume fraction problem present a linear decay of  $L^2$  error with respect to the time step. However, the convergence for

Table 3.4:  $L^2$  error with respect to the reference solution provided with time step  $\delta t = 0.01$ ,  $50 \times 10$  uniform mesh, and  $\alpha = 0.0005$  for numerical simulation in Section 3.5.2 at  $T = 10$ .

$\delta t$	$\mathbf{u}_g$	$\mathbf{u}_l$	$p$	$\alpha_g$	$c_s$	$c_k$	$c_g$
1	$5.56 \times 10^{-4}$	$5.49 \times 10^{-4}$	$1.45 \times 10^{-3}$	$9.11 \times 10^{-2}$	$9.12 \times 10^{-3}$	$3.77 \times 10^{-4}$	$1.74 \times 10^{-2}$
0.5	$2.77 \times 10^{-4}$	$2.73 \times 10^{-4}$	$7.17 \times 10^{-4}$	$4.50 \times 10^{-2}$	$6.80 \times 10^{-3}$	$2.64 \times 10^{-4}$	$8.74 \times 10^{-3}$
0.1	$4.85 \times 10^{-5}$	$4.84 \times 10^{-5}$	$1.28 \times 10^{-4}$	$8.07 \times 10^{-3}$	$3.87 \times 10^{-3}$	$2.01 \times 10^{-4}$	$1.72 \times 10^{-3}$
0.05	$2.25 \times 10^{-5}$	$2.24 \times 10^{-5}$	$5.75 \times 10^{-5}$	$3.58 \times 10^{-3}$	$3.00 \times 10^{-3}$	$1.55 \times 10^{-4}$	$8.77 \times 10^{-4}$

Table 3.5:  $L^2$  error with respect to the reference solution provided with time step  $\delta t = 0.05$ ,  $200 \times 20$  uniform mesh, and  $\alpha = 0.0005$  for numerical simulation in Section 3.5.2 at  $T = 10$ .

$(\delta t, \text{mesh})$	$\mathbf{u}_g$	$\mathbf{u}_l$	$p$	$\alpha_g$	$c_s$	$c_k$	$c_g$
(1, $25 \times 3$ )	$2.03 \times 10^{-2}$	$2.04 \times 10^{-2}$	$1.72 \times 10^{-2}$	$6.24 \times 10^{-1}$	$1.55 \times 10^{-1}$	$8.73 \times 10^{-2}$	$8.57 \times 10^{-1}$
(0.5, $50 \times 5$ )	$6.50 \times 10^{-3}$	$6.45 \times 10^{-3}$	$5.24 \times 10^{-3}$	$2.18 \times 10^{-1}$	$4.54 \times 10^{-2}$	$3.08 \times 10^{-2}$	$2.78 \times 10^{-1}$
(0.1, $100 \times 10$ )	$1.47 \times 10^{-3}$	$1.35 \times 10^{-3}$	$9.48 \times 10^{-4}$	$6.09 \times 10^{-2}$	$1.57 \times 10^{-2}$	$7.65 \times 10^{-3}$	$6.58 \times 10^{-2}$

solving the concentration profiles does not reach the expectation due to extremely low diffusion coefficients and large current densities.

Second, we conduct the convergence tests for different time step and mesh pairs. The reference solution is obtained with  $200 \times 20$  uniform mesh and  $\delta t = 0.05$  at  $T = 10$ . We always keep the time step being proportional to the mesh size. Figure 3.6 and Table 3.5 present a linear decay of  $L^2$  error with respect to the time step for each variable.

Third, the convergence tests for different time step and mesh pairs are performed until a larger final time. The reference solution is obtained with  $200 \times 20$  uniform mesh and  $\delta t = 0.3$  at  $T = 120$ . Same as the second test, we always keep the time step being proportional to the mesh size. Figure 3.7 and Table 3.6 present a nearly linear decay of  $L^2$  error with respect to the time step for each variable. In this test,  $r_g$  and  $c_k$  are of the worst convergence. Their intensity maps are given in Figures 3.8 and 3.9. Except for tests with time step  $\delta t = 1.2$ , the intensity maps for the tests with  $\delta t \leq 0.6$  present no significant difference with the reference solutions.

### Robustness for large time steps

With a large time step  $\delta t = 1$  and  $100 \times 10$  uniform mesh, the product of the maximal liquid fluid speed with the time step is around 1.5 times of the mesh size, which is optimal for the Galerkin-Characteristic method. solutions are displayed in Figure 3.10-3.15.

### CPU time

With  $\delta t = 1$  and  $100 \times 10$  uniform mesh, it took 5832 seconds to reach the final time  $T = 180$  with an Intel Core i7-8750H @ 2.20GHz. During the computation, it took 0.086% of the total

Table 3.6:  $L^2$  error with respect to the reference solution provided with time step  $\delta t = 0.3$ ,  $200 \times 20$  uniform mesh, and  $\alpha = 0.0005$  for numerical simulation in Section 3.5.2 at  $T = 120$ .

$(\delta t, \text{mesh})$	$\mathbf{u}_g$	$\mathbf{u}_l$	$p$	$\alpha_g$	$c_s$	$c_k$	$c_g$
(1.2, $50 \times 5$ )	$1.73 \times 10^{-2}$	$1.73 \times 10^{-2}$	$6.48 \times 10^{-3}$	$3.71 \times 10^{-1}$	$3.97 \times 10^{-2}$	$1.56 \times 10^{-2}$	$2.73 \times 10^{-1}$
(0.6, $100 \times 10$ )	$1.22 \times 10^{-2}$	$1.23 \times 10^{-2}$	$4.07 \times 10^{-3}$	$2.20 \times 10^{-1}$	$1.35 \times 10^{-2}$	$1.18 \times 10^{-2}$	$2.11 \times 10^{-1}$
(0.4, $150 \times 15$ )	$6.40 \times 10^{-3}$	$6.41 \times 10^{-3}$	$2.23 \times 10^{-3}$	$1.19 \times 10^{-1}$	$6.60 \times 10^{-3}$	$6.23 \times 10^{-3}$	$1.11 \times 10^{-1}$



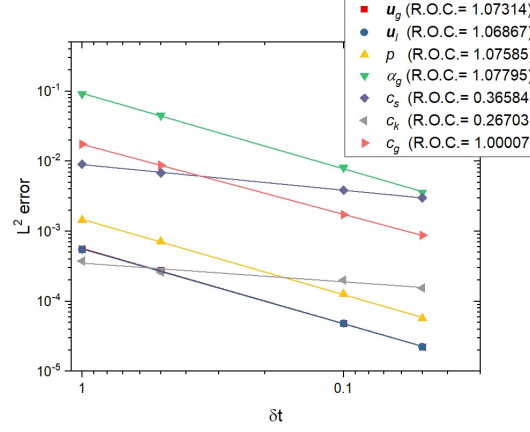


Figure 3.5: Convergence with respect to  $\delta t$  for the case described in Section 3.5.2 with fixed mesh: log-log plot of the error for each unknown; (note that the curves for  $u_g$  and  $u_l$  overlap) . R.O.C. means “Rate Of Convergence”. The reference solution is a computation with a very small time step.

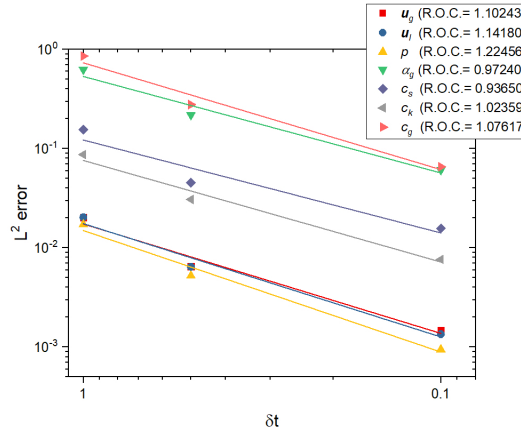


Figure 3.6: Convergence with respect to  $\delta t$  and mesh size for the case described in Section 3.5.2 (see Table 3.5 for the time step and mesh size pair): log-log plot of the error for each unknown; (note that the curves for  $u_l$  and  $u_l$  overlap) .

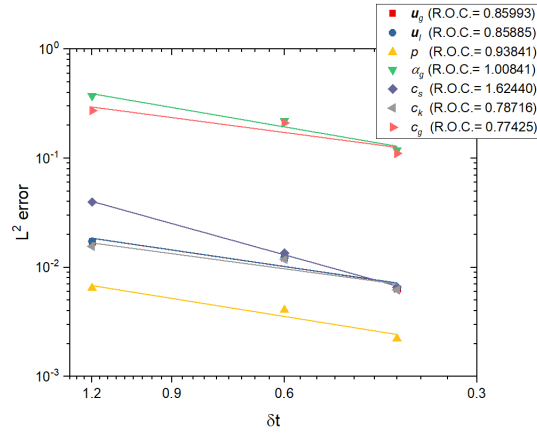
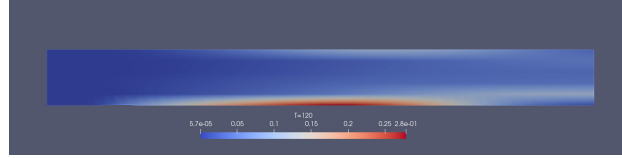
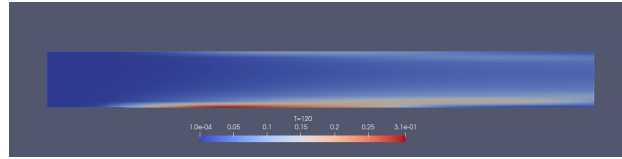


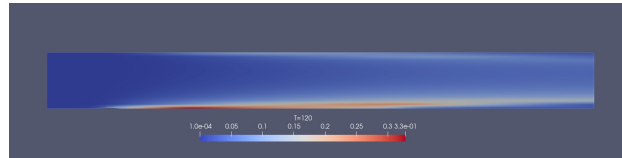
Figure 3.7: Convergence with respect to  $\delta t$  and mesh size for the case described in Section 3.5.2 (see Table 3.5 for the time step and mesh size pair): log-log plot of the error for each unknown; (note that the curves for  $u_g$  and  $c_k$  overlap and the curve of  $u_l$  is closed to them).



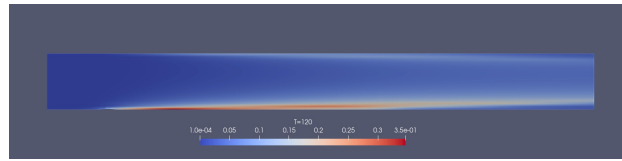
(a) Intensity map of  $r_g$  at  $t = 120$  with  $\delta t = 1.2$  and  $50 \times 5$  uniform mesh.



(b) Intensity map of  $r_g$  at  $t = 120$  with  $\delta t = 0.6$  and  $100 \times 10$  uniform mesh.

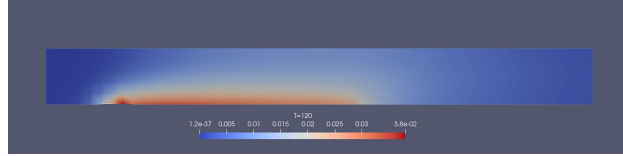


(c) Intensity map of  $r_g$  at  $t = 120$  with  $\delta t = 0.4$  and  $150 \times 15$  uniform mesh.

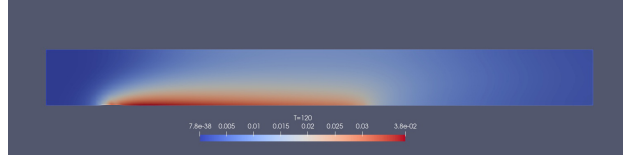


(d) Intensity map of  $r_g$  at  $t = 120$  with  $\delta t = 0.3$  and  $200 \times 20$  uniform mesh.

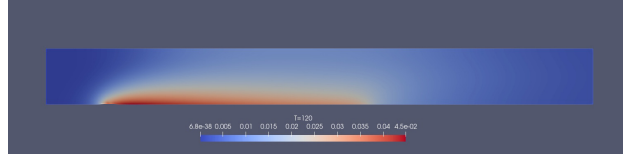
Figure 3.8: For Section 3.5.2: The intensity maps of  $r_g$  for different time step and mesh size pairs.



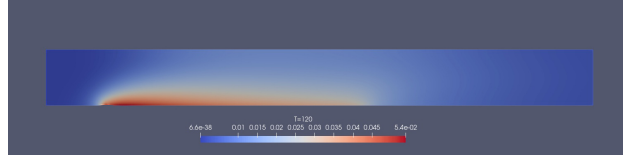
(a) Intensity map of  $c_g$  at  $t = 120$  with  $\delta t = 1.2$  and  $50 \times 5$  uniform mesh.



(b) Intensity map of  $c_g$  at  $t = 120$  with  $\delta t = 0.6$  and  $100 \times 10$  uniform mesh.

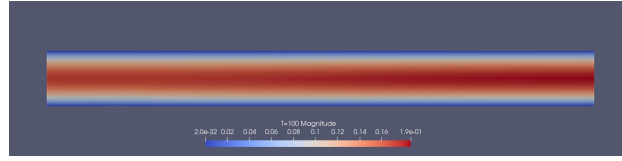
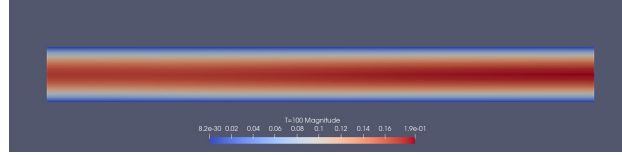


(c) Intensity map of  $c_g$  at  $t = 120$  with  $\delta t = 0.4$  and  $150 \times 15$  uniform mesh.



(d) Intensity map of  $c_g$  at  $t = 120$  with  $\delta t = 0.3$  and  $200 \times 20$  uniform mesh.

Figure 3.9: For Section 3.5.2: The intensity maps of  $c_g$  for different time step and mesh size pairs.

(a) Intensity map of  $\mathbf{u}_g$  at  $t = 100$ .(b) Intensity map of  $\mathbf{u}_l$  at  $t = 100$ .Figure 3.10: For Section 3.5.2: The velocity magnitudes of  $\mathbf{u}_g$  and  $\mathbf{u}_l$ .

CPU for solving the volume fraction problem, 7.66% for solving the chemical species transport problem and 91.93% for solving the two velocities/pressure flow problem.

The computer program is written using the **FreeFEM++** toolkit [53].

## Results

On Figure 3.10a and 3.10b the velocity vector fields  $\mathbf{u}_g$  and  $\mathbf{u}_l$  are seen to be almost parabolic in  $y$  (Poiseuille flow). but the phase change and moving boundary induce a non-zero asymmetric vertical component  $u_{2g}$  (see Figure 3.14); both play important roles for the bubble distribution. Bubble density can be inferred by analyzing  $c_g$  and  $r_g$  (see Figure 3.17). The color maps of Figure 3.11 displays a high gas volume fraction area near the top and bottom plates. Figure 3.12 shows how the steady state is established and how the electrolyte disappears in the plating region due to the plating. Figure 3.13 explains why it is always of the highest volume fraction of gaseous phase near the reacting surface. The deposition-induced movement of  $S$  is presented in Figure 3.16. Figure 3.17b shows that the region of the highest bubble density is moving away from the inlet as the electroless plating proceeds.

## 3.6 Comparison with experimental results

To validate the numerical method on a real-life problem, an experiment for reproducing the numerical study in Section 3.5.2 is conducted. Here, we shall show that the experimental result can be qualitatively fitted by the numerical simulation.

The experimental setting is described as the following: A micro-channel is enclosed by two sheet glasses of size  $8\text{ mm} \times 8\text{ mm}$  and another two of size  $8\text{ mm} \times 1\text{ mm}$ , which form a rectangular channel. The electrolyte goes in the channel from the left and exit on the right. One piece of the square sheet glasses is partially glued on a copper plate of size  $8\text{ mm} \times 4\text{ mm}$ , where the longer side of the copper plate coincides with an edge of the inlet (see Figure 3.18 for geometry setting). The inflow is set to be of average velocity  $0.115\text{ mm/s}$ . At inlet, the copper ion concentration is  $c_{s0} = 39.34\text{ mol/m}^3$  and the formaldehyde concentration is  $c_{k0} = 77.5883\text{ mol/m}^3$ . Here, the inlet concentrations  $c_{g0}$  and  $c_{k0}$  are the reference concentrations for copper ion and formaldehyde, respectively. We further define the reference concentration of the hydrogen gas to be  $c_{g0} = 1\text{ mol/m}^3$ . Other physical parameters are given by Table 3.3. Some

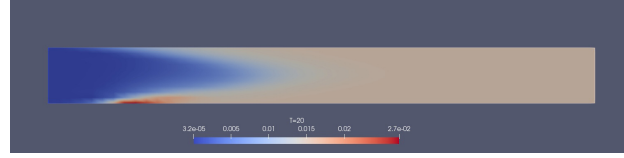
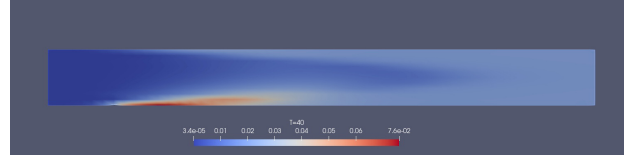
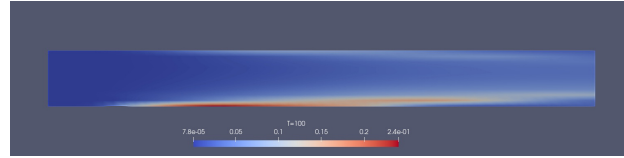
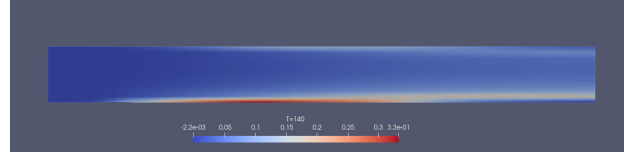
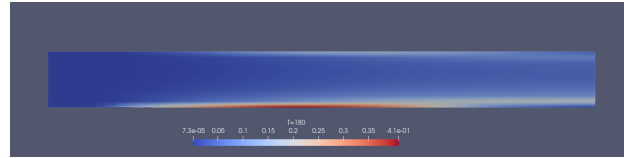
(a) Intensity map of  $r_g$  at  $t = 20$ .(b) Intensity map of  $r_g$  at  $t = 40$ .(c) Intensity map of  $r_g$  at  $t = 100$ .(d) Intensity map of  $r_g$  at  $t = 140$ .(e) Intensity map of  $r_g$  at  $t = 180$ .

Figure 3.11: For Section 3.5.2: intensity maps of the volume fraction of the gas phase  $r_g$  computed with  $\delta t = 1$  and a  $100 \times 10$  uniform mesh.

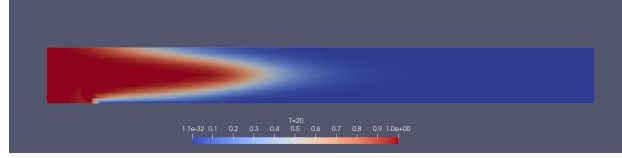
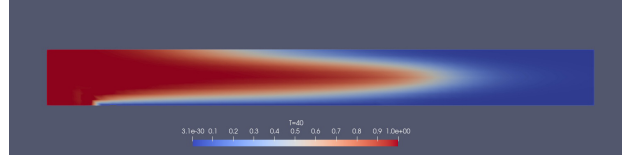
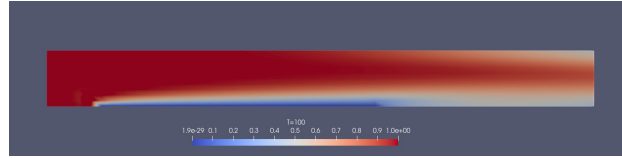
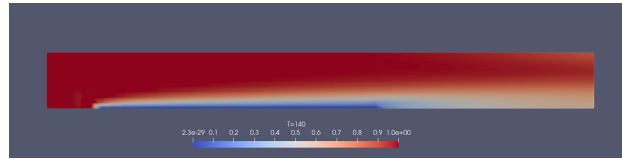
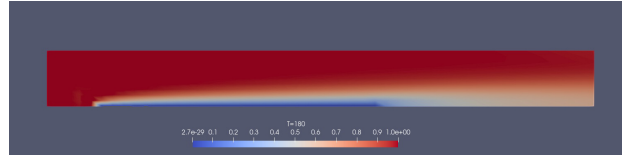
(a) Intensity map of  $c_s$  at  $t = 20$ .(b) Intensity map of  $c_s$  at  $t = 40$ .(c) Intensity map of  $c_s$  at  $t = 100$ .(d) Intensity map of  $c_s$  at  $t = 140$ .(e) Intensity map of  $c_s$  at  $t = 180$ .

Figure 3.12: For Section 3.5.2: intensity maps of the concentration electrolyte ions  $c_s$  computed with  $\delta t = 1$  and a  $100 \times 10$  uniform mesh. The blue zone in the plating region, on the lower plate shows that the electrolyte is absorbed by the plating process.

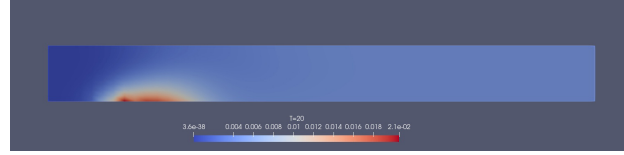
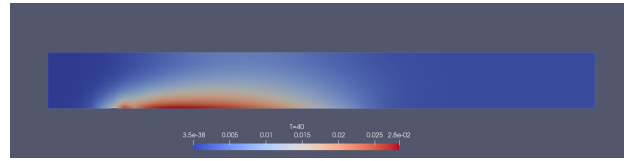
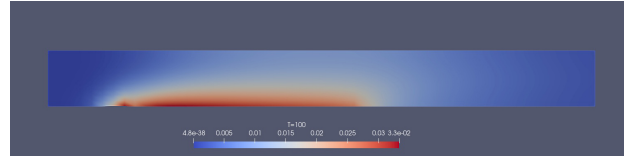
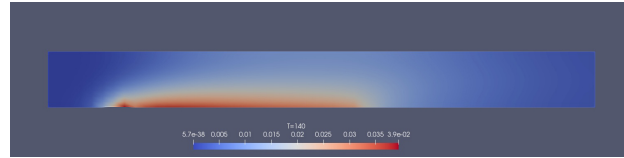
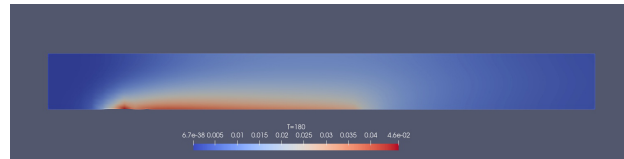
(a) Intensity map of  $c_g$  at  $t = 20$ .(b) Intensity map of  $c_g$  at  $t = 40$ .(c) Intensity map of  $c_g$  at  $t = 100$ .(d) Intensity map of  $c_g$  at  $t = 140$ .(e) Intensity map of  $c_g$  at  $t = 180$ .

Figure 3.13: For Section 3.5.2: intensity maps of the concentration of dissolved gas.

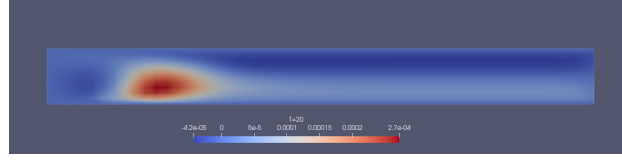
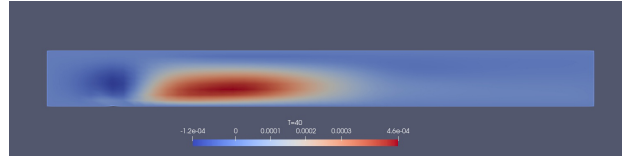
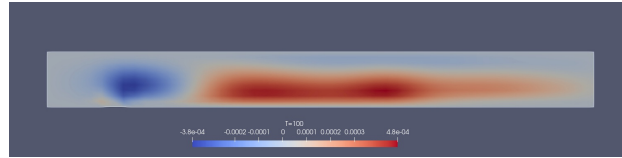
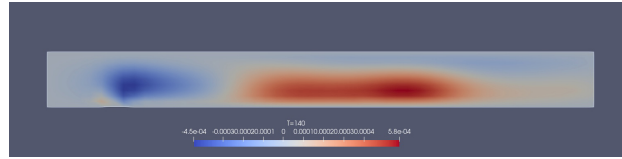
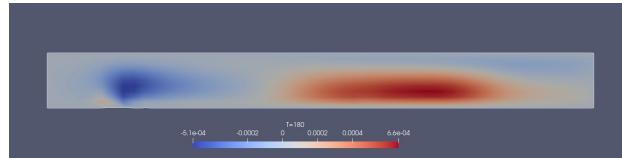
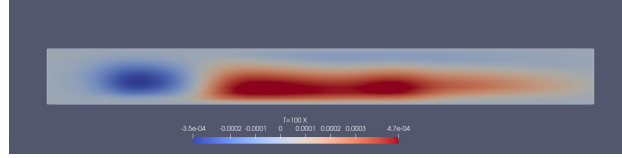
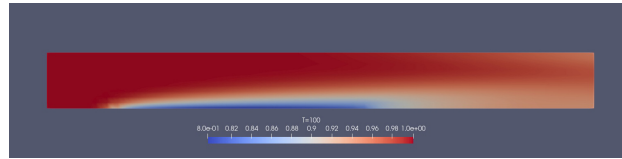
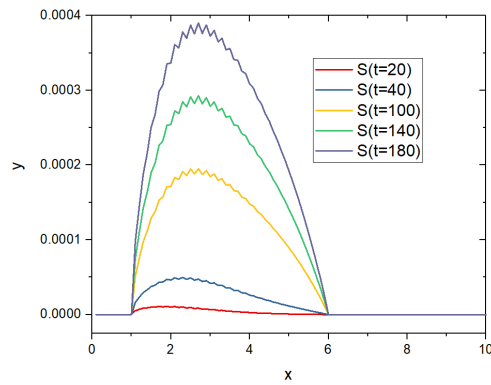
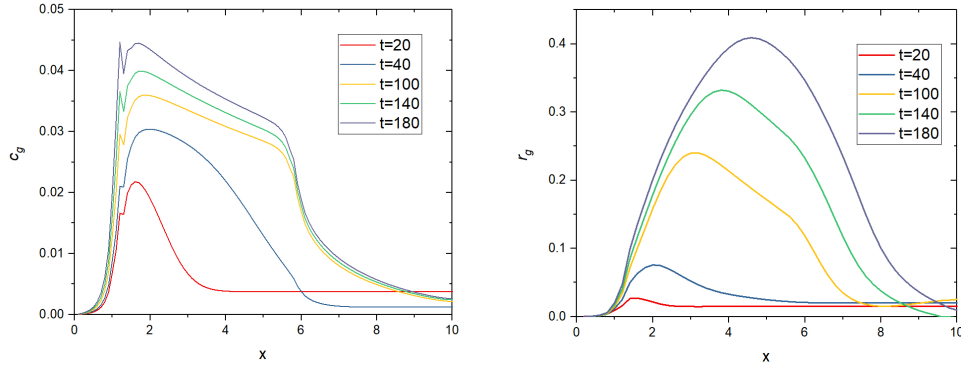
(a) Intensity map of  $u_{2g}$  at  $t = 20$ .(b) Intensity map of  $u_{2g}$  at  $t = 40$ .(c) Intensity map of  $u_{2g}$  at  $t = 100$ .(d) Intensity map of  $u_{2g}$  at  $t = 140$ .(e) Intensity map of  $u_{2g}$  at  $t = 180$ .

Figure 3.14: For Section 3.5.2: The vector fields  $\mathbf{u}_g$  and  $\mathbf{u}_l$  are very closed to Poisseuille flow. In this case, phase change and moving boundary contribute to the second component of  $\mathbf{u}_g$  (and  $\mathbf{u}_l$ ) together. The numerical test is conducted with  $\delta t = 1$  and  $100 \times 10$  uniform mesh. The intensity maps indicate the bubble rising in the red region. Indeed, there exists high gas volume fraction region near the top side (see Figure 3.11).



(a) Intensity map of  $u_{l2}$  at  $t = 100$ .(b) Intensity map of  $c_k$  at  $t = 100$ .Figure 3.15: For Section 3.5.2: Intensity maps of  $u_{l2}$  and  $c_k$  at  $t = 100$ .Figure 3.16: The thickness of the deposition is given by the motion of  $S(t)$ , plotted here at 5 instants of time, with respect to  $x$ -axis (in mm). Notice that the motion  $t \rightarrow S(t)$  is very small; the oscillations are blown-out of proportions by the scaling used in the graphic.



(a) For Section 3.5.2: Intensity map of  $c_g$  on  $S$  versus  $x$ . (b) For Section 3.5.2: Intensity map of  $r_g$  on  $S$  versus  $x$ .

Figure 3.17: Plots of  $r_g$  and  $c_g$  versus  $x$  on the reaction surface  $S$ . The gas bubble density in the plating reaction zone can be observed.

parameters, for example, reference current densities  $i_s$ ,  $i_k$ , and  $i_g$ , may not be exactly same as what are given in Table 3.3. Nevertheless, they are acceptably closed to the reality, or at least in a same order.

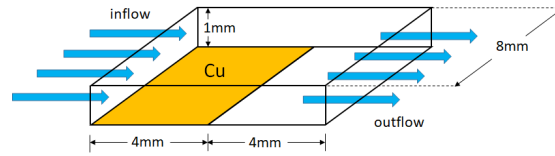


Figure 3.18: The geometry setting for both experiment and numerical simulation. Here, the yellow region indicates the copper plate glued on the sheet glass.

### 3.6.1 Experimental

To fabricate the test vehicle, a 4 inch glass wafer was first sputtered with 30 nm chromium and 200 nm copper which served as adhesion layer and seed layer, respectively. The wafer was then diced into each 8 mm  $\times$  8 mm glass dies. To ensure a significant comparison between the regions being plated or not, each test die was half immersed in SPS ( $Na_2S_2O_8$ ) solution and hydrochloric acid to remove copper and chromium layer. The glass die turned out half transparent and half coated with copper where the electroless copper plating took place. Thereafter, a fully transparent glass which was identical to the size of test die, was face-to-face aligned and bonded via using flip-chip die-bonder in order to obtain a clear observation view. Two tungsten wire which were 8 mm in length and 2 mm in diameter were glued by UV gel and placed on the periphery of the test die for the purpose of restricting the flow direction and defining the height between the dies (see Figure 3.19).

The test vehicle was then subjected to micro-fluidic system composed of a PDMS mode containing micro-fluidic channel and a bottom glass. Clips were used to sealed the micro-fluidic system and prevented the leakage of electrolyte. A peristaltic pump was used to control the flow

and connect the micro-fluidic system with silicone tube. Prior to the electroless plating, the test vehicle was immersed in 10% sulfuric acid to remove copper oxide. Finally, the electroless copper plating was conducted in a water tank controlled at  $50^\circ\text{C}$  with in-situ recording via stereomicroscope (charged coupled device digital camera CCD). The electrolyte PHE-1 Uyemura possessing the given reference concentrations  $c_{s0}$  of (complexed) copper ion and  $c_{k0}$  of formaldehyde was used for the experiment. A complete equipment setup is described in Figure 3.20.

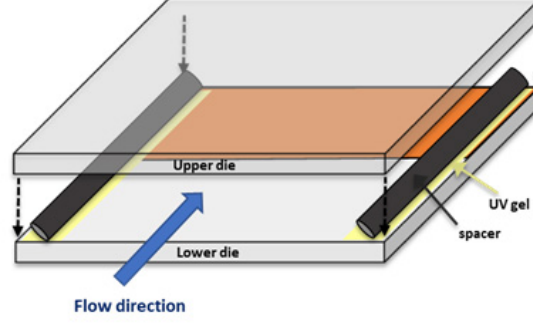


Figure 3.19: Test vehicle formation.

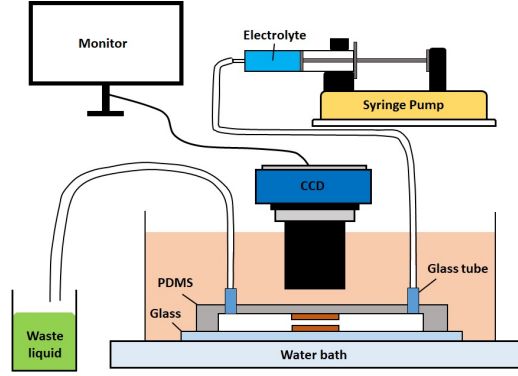
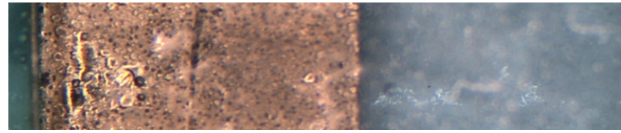


Figure 3.20: Electroless copper plating via using microfluidic system.

### 3.6.2 Results

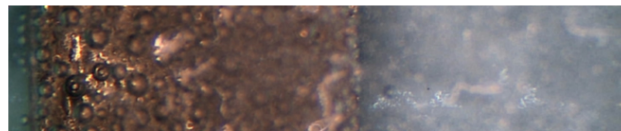
Experimental results (see Figure 3.21) show that the bubbles are not only appearing on the copper plate, but also appearing on the top. In video, one can see that there were several bubbles going to the top from the center or the bottom side of the channel. The region above the glass becomes darker with time. The simulation results (see Figure 3.11) qualitatively arrive at the same conclusion. The experiment indicates that the clustering of bubbles happens on both top side and the bottom side of the channel. Second, the numerical simulation predicts that most bubbles are generated at an early stage and near the inlet. The experiment shows that the bubble generation is more exuberant near the inlet in comparison with other regions at  $t = 20$ . This observation coincides with that of Figs 3.13 and 3.17a. The region near the inlet at  $t = 20$  is of the highest concentration of dissolving hydrogen gas. In addition, large bubbles



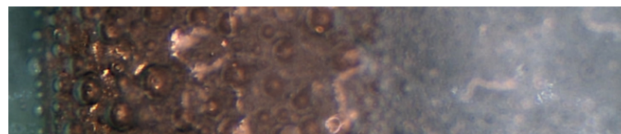
(a) The initial profile of the micro-channel.



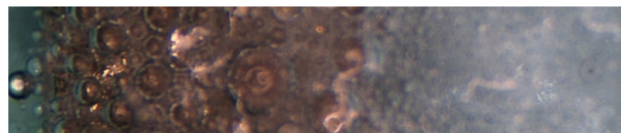
(b) micro-channel at  $t = 20$  s.



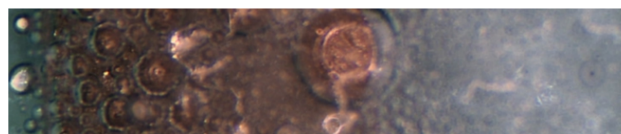
(c) micro-channel at  $t = 40$  s.



(d) micro-channel at  $t = 100$  s.



(e) micro-channel at  $t = 140$  s.



(f) micro-channel at  $t = 180$  s.

Figure 3.21: The pictures are taken from the top side and the region near the center between two  $8\text{ mm} \times 1\text{ mm}$  sheet glasses. The brown region is covered by the copper plate, where the surface reaction occurs.

were observed at the back end of the copper plates (i.e. region near  $(x,y) = (6,0)$  corresponding Figure 3.1), which is also the case in Figure 3.17b.

### 3.6.3 Discussion

For an electroless plating process accompanying gas generation, the bubble distribution with respect to time, in the micro-channel, is the most important index for evaluating the quality of deposition. To measure it quantitatively, a high-quality optical system installed in the micro-channel is indispensable. For example, several types of fiber optical probe have been used to measure the particle (or bubble) size and distribution in a channel flow (or micro-channel flow) [23, 12, 62, 82]. However, such optical system is difficult to be installed in our case because there is no appropriate place to setup the light source and the detector in the micro-channel. The signal interference caused by the copper plate or glued gel on two sides is almost inevitable.

## 3.7 Conclusion

The numerical simulation of an electroless plating is difficult for two reasons: the multi-phase modeling and the nonlinearities. We have proposed a phase averaged liquid-gas two fluid velocities/one pressure system combined with phase densities and chemical concentration equations. The nonlinearities being similar to those of the Navier-Stokes equations, we have used a semi-Eulerian time discretization leading to a generalized Stokes operator for the two velocities/one pressure system; the inf-sup saddle point theorem has lead to a proof of stability and well posedness of the discretized system by the Hood-Taylor finite element method. The two phase flow model is compatible with single phase models when the volume fraction of gas and the concentration of the gas in the liquid phase are set to zero. The model is also compatible with the one dimensional model proposed in [66]. The numerical results confirm the robustness of the method. To validate the model a real life experiment has been performed. The numerical results agree qualitatively with the experiment for the repartition of bubbles near the plating boundary. We believe that in the future the computer code will be used to design industrial and experimental systems. However, as to the measurement of the deposition rate, It takes at least one hour to obtain an observable thickness of plating. In this case, bubbles have accumulated everywhere in the micro-channel and there is ground for an extension of the present code with a level set or phase field model which tracks the liquid to gas interface. To establish a mathematical model suitable for a larger time simulation is left as a future work.

## 3.A Estimation of the interfacial terms

Let  $V_0$  be a local volume to be observed which is occupied by gas and liquid. In a liquid-gas two phase system, we have  $A_l = A_g$  and further  $\rho_l(\mathbf{w}_l - \mathbf{u}_l) \cdot \mathbf{n}_l = -\rho_g(\mathbf{w}_g - \mathbf{u}_g) \cdot \mathbf{n}_g$  on the interface. If the size of each single bubble in the electrolyte is small enough, then we can assume that the bubbles are spherical. Assuming that there is a typical radius for all bubbles  $R_B > 0$  such that  $1/R_B^2$  is the average of  $1/R^2$  among all bubbles in the system, the growth rate of bubbles governed by the local mass loss prescribed by Eq. (3.3) can be computed by the relation

$$4\pi R_B^2 N_q \frac{dR}{dt} = \int_{V_0} \frac{\dot{S}_g}{\rho_g} dV, \quad (3.75)$$

where  $N_q$  is the amount of bubbles in a local volume  $V_0$ . Therefore, we have the following formulae on  $A_g$  and  $A_l$ , respectively

$$(\mathbf{u}_g - \mathbf{w}_g) \cdot \mathbf{n}_g = -\frac{1}{4\pi N_q R^2} \int_{V_0} \frac{\dot{S}_g}{\rho_g} dV \quad (3.76)$$

$$(\mathbf{u}_l - \mathbf{w}_l) \cdot \mathbf{n}_l = \frac{1}{4\pi N_q R^2} \int_{V_0} \frac{\dot{S}_g}{\rho_l} dV. \quad (3.77)$$

The quantity  $R_B$  is useful when the fluid velocity is large enough so that each bubble won't stay at the observed physical domain, because every bubble hasn't been far from the state that is just after nucleation.

Given a small cube  $V_0$  of size  $|V_0| = d \times d \times d$  and a typical radius  $R_B$ , the ratio of its surface area and volume is  $\frac{4\pi N_q R_B^2}{d^3}$ , where  $N_q$  can be estimated by

$$N_q = \frac{r_g d^3}{\frac{4}{3}\pi R_B^3} \quad (3.78)$$

Therefore, if  $d$  is small enough so that the physical quantities in  $\mathbf{F}_\alpha$  defined in Section 3.2.3 can be assumed uniform, then we have the approximation

$$(3.79)$$

$$\mathbf{F}_l \approx \left( \frac{4\pi N_q R_B^2}{d^3} \right) \cdot \rho_l \cdot \left( -\frac{d^3 \dot{S}_g}{4\pi N_q R_B^2 \rho_l} \right) \mathbf{u}_l = -\dot{S}_g \mathbf{u}_l = \dot{S}_l \mathbf{u}_l. \quad (3.80)$$

Similarly,

$$\mathbf{F}_g \approx \dot{S}_g \mathbf{u}_g \quad (3.81)$$

The same approximation can be applied to  $G_j$  occurring at (3.5) and (3.6):

$$G_j \approx \dot{S}_l c_j, \quad j = s, k, \quad G_g \approx \dot{S}_l c_g - M_g K \rho_l r_l (c_g - c_{sat})^+ \quad (3.82)$$



# Appendix A

## Preliminaries and notations

### A.1 Lebesgue spaces $L^p(\Omega)$ and Sobolev spaces $W^{k,p}(\Omega)$

#### A.1.1 $L^p$ space

Let  $1 \leq p \leq \infty$  and  $\Omega \subset \mathbb{R}^d$  a bounded domain. We denote by  $L^p(\Omega)$  the set of all measurable functions from  $\Omega$  to  $\mathbb{C}$  or  $\mathbb{R}$  which satisfy

$$\|f\|_p := \begin{cases} \left( \int_{\Omega} |f|^p dx \right)^{1/p} < \infty & 1 \leq p < \infty; \\ \text{ess sup}_{x \in \Omega} |f| & p = \infty. \end{cases} \quad (\text{A.1})$$

In particular,  $L^2(\Omega)$  is a Hilbert space with the inner product  $(\cdot, \cdot)$  defined by

$$(f, g) := \int_{\Omega} f(x) \overline{g(x)} dx, \quad f, g \in L^2(\Omega), \quad (\text{A.2})$$

which induces the norm  $\|\cdot\|_0$ .

#### A.1.2 Sobolev space

Let  $k$  be a natural number,  $\alpha = (\alpha_1, \dots, \alpha_d)$  a multi-index with norm  $|\alpha| = \alpha_1 + \dots + \alpha_d$ . We define

$$D^{\alpha} f = \frac{\partial^{|\alpha|} f}{\partial x_1^{\alpha_1} \dots \partial x_d^{\alpha_d}}$$

The Sobolev space  $W^{k,p}(\Omega)$  is defined as

$$W^{k,p}(\Omega) := \{f \in L^p(\Omega) : D^{\alpha} f \in L^p(\Omega) \ \forall |\alpha| \leq k\} \quad (\text{A.3})$$

A common way to define the norm of  $W^{k,p}(\Omega)$  is

$$\|f\|_{W^{k,p}(\Omega)} := \begin{cases} \left( \sum_{|\alpha| \leq k} \|D^{\alpha} f\|_{L^p(\Omega)}^p \right)^{\frac{1}{p}} & 1 \leq p < \infty; \\ \max_{|\alpha| \leq k} \|D^{\alpha} f\|_{L^{\infty}(\Omega)} & p = \infty. \end{cases} \quad (\text{A.4})$$



For the particular case  $p = 2$ , the space  $H^k(\Omega) := W^{k,2}(\Omega)$  is a Hilbert space. Moreover, we denote by  $H_{\Gamma_D}^1(\Omega)$  the closed subspace of  $H^1(\Omega)$  defined by

$$H_{\Gamma_D}^1(\Omega) := \{f \in H^1(\Omega) : f|_{\Gamma_D} = 0\}. \quad (\text{A.5})$$

If the number  $k$  is non-integer, we define the fractional Sobolev space in two cases: If  $0 < k < 1$ , we define  $W^{k,p}$  for  $1 \leq p < \infty$  by

$$W^{k,p}(\Omega) := \left\{ f \in L^p(\Omega) : \frac{|f(x) - f(y)|}{|x - y|^{\frac{d}{p} + k}} \in L^p(\Omega \times \Omega) \right\} \quad (\text{A.6})$$

which endowed with the norm

$$\|f\|_{W^{k,p}(\Omega)} := \left( \int_{\Omega} |f|^p dx + \int_{\Omega} \int_{\Omega} \frac{|f(x) - f(y)|^p}{|x - y|^{\frac{d}{p} + k}} dx dy \right)^{\frac{1}{p}}. \quad (\text{A.7})$$

When  $k > 1$  and it is not an integer, we write  $k = m + s$ , where  $m$  is an integer and  $0 < s < 1$ . The space  $W^{k,p}(\Omega)$  is defined by

$$W^{k,p}(\Omega) := \{f \in W^{m,p} : D^{\alpha} f \in W^{s,p} \ \forall \alpha \text{ s.t. } |\alpha| = m\}. \quad (\text{A.8})$$

The above space is equipped with the norm

$$\|f\|_{W^{k,p}(\Omega)} := \left( \|f\|_{W^{m,p}(\Omega)}^p + \sum_{|\alpha|=m} \|D^{\alpha} f\|_{W^{s,p}(\Omega)}^p \right)^{\frac{1}{p}}. \quad (\text{A.9})$$

In particular,  $H^k(\Omega) := W^{k,2}(\Omega)$  is again a Hilbert space when  $k$  is non-integer.

For convenience, we denote the norm of  $H^k(\Omega)$  by  $\|\cdot\|_k$  for real  $k \geq 0$ .

### A.1.3 Traces

**Theorem A.1.1** Let  $\Omega \subset \mathbb{R}^d$  be bounded with Lipschitz boundary. Then there exists a bounded linear operator  $T : W^{1,p}(\Omega) \rightarrow L^p(\partial\Omega)$  such that

$$\begin{aligned} Tu &= u|_{\partial\Omega}, \quad u \in W^{1,p}(\Omega) \cap C(\overline{\Omega}) \\ \|Tu\|_{L^p(\partial\Omega)} &\leq c(p, \Omega) \|u\|_{W^{1,p}(\Omega)}, \quad u \in W^{1,p}(\Omega) \end{aligned} \quad (\text{A.10})$$

**Remark A.1.1** For  $1 < p < \infty$ , the trace operator  $T$  maps maps  $W^{1,p}(\Omega)$  continuously onto the space  $W^{1-\frac{1}{p},p}(\partial\Omega)$ .

### A.1.4 Bochner space

Given  $I := [0, T]$  a time interval and a Sobolev space  $W^{k,p}(\Omega)$ , the Bochner space  $L^r(I; W^{k,p}(\Omega))$  is the space of all measurable function  $u : I \rightarrow W^{k,p}(\Omega)$  such that the associated norm is finite:

$$\begin{aligned} \|u\|_{L^r(I; W^{k,p}(\Omega))} &:= \left( \int_0^T \|u(t)\|_{W^{k,p}(\Omega)}^r dt \right)^{\frac{1}{r}} < +\infty, \quad 1 \leq r < \infty \\ \|u\|_{L^\infty(I; W^{k,p}(\Omega))} &:= \operatorname{ess\,sup}_{t \in I} \|u(t)\|_{W^{k,p}(\Omega)} < +\infty, \quad r = \infty. \end{aligned} \quad (\text{A.11})$$

## A.2 Weighted Sobolev space

**Definition A.2.1 (Weighted space  $L_\rho^p(\Omega, d, m)$  and  $W_\rho^{1,p}(\Omega, d, m)$ )** Let  $(\Omega, d, m)$  be a metric measure space, where  $m$  is a locally finite Borel regular measure on  $\Omega$ . Let  $p > 1$  and  $\rho : \Omega \rightarrow [0, \infty]$  a Borel function satisfying  $\rho^{-1} \in L^{\frac{1}{p-1}} m$ ; we define the weighted space  $L^p(\Omega, d, m)$  and sobolev space  $W_\rho^{1,p}(\Omega, d, m)$  by

$$L_\rho^p(m) := \left\{ f \in L^1(\Omega, d, m) \mid \int_\Omega |f|^p \rho dm < +\infty \right\},$$

$$W_\rho^{1,p}(m) := \left\{ f \in W^{1,1}(\Omega, d, m) \mid \int_\Omega |f|^p \rho dm + \int_\Omega |\nabla f|^p \rho dm < +\infty \right\},$$

respectively. The above spaces are endowed with the norms

$$\|f\|_{L_\rho^p}^p := \int_\Omega |f|^p \rho dm + \int_\Omega |\nabla f|^p \rho dm.$$

$$\|f\|_{W_\rho^{1,p}}^p := \int_\Omega |f|^p \rho dm + \int_\Omega |\nabla f|^p \rho dm.$$

If  $\Omega \subset \mathbb{R}^n$  endowed with standard Euclidean metric, we shorten the notations by  $L_\rho^p(\Omega) := L_\rho^p(\Omega, d, m)$ ,  $W_\rho^{1,p}(\Omega) := W_\rho^{1,p}(\Omega, d, m)$ , respectively

**Proposition A.2.1**  $\forall p > 1$ , the weighted Sobolev space  $(W_\rho^{1,p}(\Omega, d, m), \|\cdot\|_\rho)$  is a Banach space whenever  $\rho^{-1} \in L^{\frac{1}{p-1}}(\Omega)$

**Definition A.2.2 (Doubling)** A locally finite Borel measure  $m$  on  $(\Omega, d)$  is doubling if it gives finite positive measure to balls and there is a constant  $C > 0$  such that

$$m(B(x, 2r)) \leq C m(B(x, r)), \quad \forall x \in \Omega, \quad r > 0$$

**Definition A.2.3 ( $p$ -Poincaré)** For  $p \in [1, \infty)$ , we say that a  $p$ -Poincaré inequality holds for Lipschitz functions if there are constants  $\tau, \Lambda > 0$  such that  $\forall f \in \text{Lip}(\Omega), \forall x \in \text{supp}(m), r > 0$ , the following inequality holds:

$$\frac{1}{m(B(x, r))} \int_{B(x, r)} |f - f_{B(x, r)}| dm \leq \tau \left( \frac{1}{m(B(x, \Lambda r))} \int_{B(x, \Lambda r)} |\nabla f|^p dm \right)^{\frac{1}{p}},$$

where

$$f_A := \frac{1}{m(A)} \int_A f dm.$$

**Definition A.2.4** A doubling metric measure space satisfying  $p$ -Poincaré inequality is called  $\text{PI}_p$  space.

**Remark A.2.1** Euclidean space endowed with normal euclidean distancing is  $\text{PI}_p$  for all  $p \geq 1$ .

**Theorem A.2.1** [3] Suppose that  $(\Omega, d, m)$  is a  $\text{PI}_1$  metric measure space,  $\rho \in L_{loc}^1(m)$  and  $\rho^{-1} \in L^{\frac{1}{p-1}}(m)$ . Then  $W_\rho^{1,p}(\Omega, d, m)$  is reflexive for all  $p > 1$ .

**Corollary A.2.1** Let  $\Omega \subset \mathbb{R}^d$  be a open bounded domain,  $W_\rho^{1,p}$  is a reflexive Banach space if  $p > 1$ ,  $\rho \in L_{loc}^1(\Omega)$ , and  $\rho^{-1} \in L^{\frac{1}{p-1}}(\Omega)$ .

**Remark A.2.2** Let  $\Omega \subset \mathbb{R}^d$  and  $p = 2$ , we denote  $W_\rho^{1,p}(\Omega)$  by  $H_\rho^1(\Omega)$ , which is a Hilbert space endowed with the inner product

$$(u, v)_{\rho,1} = \int_{\Omega} u(x)v(x)\rho(x)dx + \int_{\Omega} (\nabla u(x) \cdot \nabla v(x))\rho(x)dx.$$

We also denote the inner product for  $L_\rho^2(\Omega)$  by

$$(u, v)_{\rho,0} = \int_{\Omega} u(x)v(x)\rho(x)dx.$$

The norm of  $H_\rho^k(\Omega)$ ,  $k \in \mathbb{N} \cup \{0\}$  is denoted by  $\|\cdot\|_{\rho,k}$ .

**Theorem A.2.2 (compact embedding)** [48] Let  $\Omega \subset \mathbb{R}^d$ ,  $1 \leq s \leq r < \frac{dq}{d-q}$ ,  $q \leq p$ ,  $1 < p < +\infty$ , and

$$K(w) := \max \left\{ \|w^{-\frac{1}{p}}\|_{L^{\frac{pq}{p-q}}(\Omega)}, \|w^{\frac{1}{s}}\|_{L^{\frac{rs}{r-s}}(\Omega)} \right\} < +\infty. \quad (\text{A.12})$$

Note that we take  $+\infty$  if  $p - q = 0$  or  $r - s = 0$  in (A.12). Then the embedding operator

$$i : W_w^{1,p}(\Omega) \hookrightarrow L_w^s(\Omega)$$

is a compact operator. For  $r = dq/(d - q)$ , the embedding operator  $i$  is bounded only.

### A.3 Weak convergence in Banach spaces

**Lemma A.3.1** Let  $E$  be a Banach space,  $\|\cdot\|$  its norm, and  $f_n : E \rightarrow \mathbb{R}$  a sequence of functions for  $n = 1, 2, \dots$ . If  $f_n$  is equicontinuous and pointwisely convergent on a dense subset  $D \subset E$ , then  $f_n$  is pointwisely convergent everywhere.

*Proof.* Let  $a \in E$ . Since  $D$  is dense in  $E$ , there is a  $b \in D$  such that for every  $\epsilon$  there is a  $\delta$  such that  $\|a - b\| < \delta$  and  $|f_n(b) - f_n(a)| < \frac{\epsilon}{3}$ . For any  $m > n$ , we have

$$\begin{aligned} |f_m(a) - f_n(a)| &\leq |f_m(a) - f_m(b)| + |f_m(b) - f_n(b)| + |f_n(b) - f_n(a)| \\ &< \frac{2\epsilon}{3} + |f_m(b) - f_n(b)| \end{aligned}$$

But  $f_n(b)$  is convergent, it is shown that  $f_n(a)$  is a Cauchy sequence. Q.E.D.

**Lemma A.3.2** Let  $E$  be a normed space,  $\|\cdot\|$  its norm and  $\|\cdot\|_{E'}$  the norm of its dual space. Let  $x_n$  be a sequence in  $E$  for  $n = 1, 2, \dots$ ,  $x \in E$ . The followings are equivalent:

- (i)  $x_n \rightarrow x$  in  $E$  weakly
- (ii)  $x_n$  is bounded and for all  $S \subset E'$  such that  $\overline{\text{span } S} = E'$  satisfies  $\lim_{n \rightarrow \infty} f(x_n) = f(x)$  for all  $f \in S$ .

*Proof.* (i) $\Rightarrow$ (ii). Assuming that  $x_n \rightarrow x$  in  $E$  weakly, then  $x_n$  is bounded. Moreover, for all  $f \in E'$ , we have  $\lim_{n \rightarrow \infty} f(x_n) = f(x)$ . Hence for all  $S \subset E'$  such that  $\overline{\text{span } S} = E'$  we have  $\lim_{n \rightarrow \infty} f(x_n) = f(x)$  for all  $f \in S$ .

(ii) $\Rightarrow$ (i). Assume that  $\|x_n\|$  is bounded by some constant  $M > 0$  and for all  $S \subset E'$  such that  $\overline{\text{span } S} = E'$  satisfies  $\lim_{n \rightarrow \infty} f(x_n) = f(x)$  for all  $f \in S$ . Take arbitrary  $g \in \text{span } S$ , then

$g = \sum_{k=1}^m \alpha_k f_k$  for  $\alpha_k \in \mathbb{R}$  and  $f_k \in S$ . This gives us  $\lim_{n \rightarrow \infty} g(x_n) = g(x)$ . Now, take arbitrary  $g \in E' = \overline{\text{span } S}$ , then  $g = \lim_{k \rightarrow \infty} g_k$  for some sequence  $g_k$  in  $\text{span } S$ . Fix  $\epsilon > 0$ . Since  $g = \lim_{k \rightarrow \infty} g_k$ , there is  $K \in \mathbb{N}$  such that  $\|g - g_k\|_{E'} \leq \epsilon$  for all  $k > K$ . Then

$$\begin{aligned} |g(x_n) - g(x)| &\leq |g(x_n) - g_k(x_n)| + |g_k(x_n) - g_k(x)| + |g_k(x) - g(x)| \\ &\leq \|g - g_k\|_{E'} \|x_n\| + |g_k(x_n) - g_k(x)| + \|g_k - g\|_{E'} \|x\| \\ &\leq \epsilon M + |g_k(x_n) - g_k(x)| + \epsilon \|x\| \end{aligned} \quad (\text{A.13})$$

We take a limit  $n \rightarrow \infty$  in the above inequality, then

$$\limsup_{n \rightarrow \infty} |g(x_n) - g(x)| \leq \epsilon M + \lim_{n \rightarrow \infty} |g_k(x_n) - g_k(x)| + \epsilon \|x\|$$

Since  $g_k \in \text{span } S$ , we have  $\lim_{n \rightarrow \infty} |g_k(x_n) - g_k(x)| = 0$  and we get

$$\limsup_{n \rightarrow \infty} |g(x_n) - g(x)| \leq \epsilon M + \epsilon \|x\|.$$

Since  $\epsilon > 0$  is arbitrary, we obtain  $\limsup_{n \rightarrow \infty} |g(x_n) - g(x)| = 0$ . This implies that  $\lim_{n \rightarrow \infty} g(x_n) = g(x)$ .

Since  $g \in E'$  is arbitrary, the proof is completed. Q.E.D.

**Lemma A.3.3** Let  $X$  be a Banach space,  $D$  a dense subset of  $X'$ ,  $x_n, n = 1, 2, \dots$  the bounded sequence in  $X$ . If  $g(x_n) \rightarrow g(x)$  for all  $g \in D$ , then  $x_n \rightarrow x$  weakly in  $X$ .

*Proof.* If  $x_n$  is a bounded sequence in  $X$ , it is an equicontinuous sequence as a sequence of functions  $X' \rightarrow \mathbb{R}$ . And  $x_n$  is pointwisely convergent on  $D$  by the hypothesis. Using Lemma A.3.1,  $x_n$  is pointwisely convergent. By Lemma A.3.2, since  $x_n$  is bounded in norm by the hypothesis, we conclude that  $x_n$  is weakly convergent to  $x$  in  $X$ . Q.E.D.

**Lemma A.3.4** Let  $X, Y$  be two normed space and  $T : X \rightarrow Y$  the bounded linear operator. If  $x_n \rightarrow x$  weakly in  $X$ , then  $Tx_n \rightarrow Tx$ .

*Proof.* Let  $y^* \in Y'$ . We can define  $x^* = y^*T \in X'$ . So

$$y^*(Tx_n) = (y^*T)(x_n) = x^*(x_n) \rightarrow x^*(x) = (y^*T)(x) = y^*(Tx).$$

Q.E.D.

**Corollary A.3.1** Let  $\Gamma \subset \partial\Omega$ . There is a trace operator  $Tr : L^2(0, T; H^1(\Omega)) \rightarrow L^2(0, T; H^{\frac{1}{2}}(S))$  such that: If  $x_n \rightarrow x$  weakly in  $L^2(0, T; H^1(\Omega))$ , then  $Trx_n \rightarrow Trx$  weakly in  $L^2(0, T; H^{\frac{1}{2}}(\Gamma))$ .

*Proof.* By Section 5.7 in [117], there exists a trace operator  $Tr : L^2(0, T; H^1(\Omega)) \rightarrow L^2(0, T; H^{\frac{1}{2}}(\Gamma))$  which is linear and bounded. By Lemma A.3.4, the proof is completed. Q.E.D.



## Appendix B

# A simplified model with surface reaction

We assume that  $\Omega \subset \mathbb{R}^d$  be a bounded open domain. For Sobolov space, the norm of  $W^{k,p}(\Omega)$  space is denoted by  $\|\cdot\|_{k,p}$  for  $p > 0$ ,  $k \geq 0$ . If  $p = 2$ , the norm is denoted by  $\|\cdot\|_k$ . For weighted Sobolev space, we denote the norm of  $H_\rho^k(\Omega)$  by  $\|\cdot\|_{\rho,k}$  for  $k \in \mathbb{N}$ ,  $\rho$  any function satisfying  $\rho, \frac{1}{\rho} \in L^1(\Omega)$ . If  $k = 0$ , we denote the norm of  $L_\rho^2(\Omega)$  by  $\|\cdot\|_\rho$  for simplicity. We denote the inner product for  $L_\rho^2(\Omega)$  by  $(\cdot, \cdot)_\rho$ . For convenience, we denote the generic constant by  $C$  or  $C_j$ ,  $j = 1, 2, \dots$

### B.1 Modeling equations

We assume that there are two chemical species  $s$  and  $k$  involving in the surface reaction in terms of the mixed potential (see (3.20)). Let  $E_j$  be the constant with subscripts  $j = s, k$  representing the ion to be plated and the anodic ion involving in the surface reaction, respectively. Without loss of generality, we assume that  $0 > E_s > E_k$ . For the physical system, we assume that the chemical reaction satisfying electron balance on the reaction surface  $S \subset \partial\Omega$ , the convective effect in system (3.26)-(3.26) is negligible, and the densities satisfy  $\rho_l \gg \rho_g > 0$ . For simplicity, we further assume that the saturation concentration can be neglected. That is, we require that

$$\mathbf{u}_g = \mathbf{u}_l = 0, \quad c_{sat} = 0. \quad (\text{B.1})$$

Employing (B.1) into (3.3), we get

$$\partial_t r_l = -\frac{K}{\tilde{\rho}_g} r_l c_g, \quad (\text{B.2})$$

where  $\frac{1}{\tilde{\rho}_g} := \frac{1}{\rho_g} - \frac{1}{\rho_l}$ . The assumption (B.1) tells us that the momentum balance equations (3.27) are dropped. The remaining equations (3.5) with the assumption (B.1) can be rewritten as

$$\begin{aligned} r_l \partial_t c_j - D_j \nabla \cdot (r_l \nabla c_j) &= 0, \quad j \neq g \\ r_l \partial_t c_g - D_g \nabla \cdot (r_l \nabla c_g) + \frac{K_g M_g}{\rho_l} r_l c_g &= 0 \end{aligned} \quad (\text{B.3})$$

Since there are only two chemical species  $s$  and  $k$  involving in the surface reaction, (B.2), (B.3) and the boundary conditions (3.19)-(3.20) with electrical neutrality assumption lead to the system:

$$\begin{aligned} \partial_t r_l &= -\frac{K}{\rho_g} r_l c_g, \quad \text{in } \Omega \times (0, T], \\ r_l \partial_t c_g - D_g \nabla \cdot (r_l \nabla c_g) + \frac{K_g M_g}{\rho_l} r_l c_g &= 0, \quad \text{in } \Omega \times (0, T], \\ r_l \partial_t c_s - D_s \nabla \cdot (r_l \nabla c_s) &= 0, \quad \text{in } \Omega \times (0, T], \\ r_l \partial_t c_k - D_k \nabla \cdot (r_l \nabla c_k) &= 0, \quad \text{in } \Omega \times (0, T], \end{aligned} \quad (\text{B.4})$$

subject to the boundary conditions

$$\begin{aligned} -D_s \frac{\partial c_s}{\partial \mathbf{n}} &= \frac{|I_s|}{z_s F}, \quad -D_k \frac{\partial c_k}{\partial \mathbf{n}} = \frac{|I_k|}{z_k F}, \quad -D_g \frac{\partial c_g}{\partial \mathbf{n}} = -\frac{\beta |I_s|}{z_s F} \quad \text{on } S, \\ \frac{\partial c_s}{\partial \mathbf{n}} &= \frac{\partial c_k}{\partial \mathbf{n}} = \frac{\partial c_g}{\partial \mathbf{n}} 0, \quad \text{on } \partial\Omega \setminus S \times (0, T] \end{aligned} \quad (\text{B.5})$$

for some constant  $\beta > 0$ . The initial conditions  $r_l(0) = r_l^0$ ,  $c_s(0) = c_s^0$ ,  $c_k(0) = c_k^0$ ,  $c_g(0) = c_g^0$  are all in  $H^1(\Omega)$  satisfying

$$0 < c_s^0, c_k^0, c_g^0 \leq 1, \quad 0 < \epsilon < r_l^0 \leq 1 \quad \text{in } \Omega \quad (\text{B.6})$$

for some constant  $\epsilon > 0$ . In the above,  $I_s$  and  $I_k$  satisfy (3.20) with  $j = s, k$  respectively and we further assume that  $\gamma_s = \gamma_k = 1$ . For electron balance, we have the constrain:

$$I_s + I_k = 0, \quad \text{on } S. \quad (\text{B.7})$$

We shall note that we replace  $\tilde{\rho}_g$  with  $\rho_g$  in (B.4) by an abuse of notation.

**Remark B.1.1** In (B.4), we employ  $c_g$  instead of  $c_g^+$  in the second term of the first equation and the third term of the second equation. We will show that  $c_g$  is nonnegative with a proper initial condition.

## B.2 Time-discrete problem

Let  $N > 0$  be an integer and  $\delta t = T/N$  be the time step. To study the existence and the stability of (B.4)-(B.7), we consider the time-discrete problem:

$$\begin{aligned} \frac{r_l^{m+1} - r_l^m}{\delta t} &= -\frac{K_g}{\rho_g} r_l^{m+1} c_g^m \\ \frac{r_l^{m+1} c_g^{m+1} - r_l^{m+1} c_g^m}{\delta t} - \nabla \cdot (D_g r_l^{m+1} \nabla c_g^{m+1}) + \frac{M_g K_g}{\rho_l} r_l^{m+1} c_g^{m+1} &= 0 \\ \frac{r_l^{m+1} c_s^{m+1} - r_l^{m+1} c_s^m}{\delta t} - \nabla \cdot (D_s r_l^{m+1} \nabla c_s^{m+1}) &= 0 \\ \frac{r_l^{m+1} c_k^{m+1} - r_l^{m+1} c_k^m}{\delta t} - \nabla \cdot (D_k r_l^{m+1} \nabla c_k^{m+1}) &= 0 \end{aligned} \quad (\text{B.8})$$

with boundary conditions on  $S$ :

$$-D_s \frac{\partial c_s^{m+1}}{\partial \mathbf{n}} = \frac{1}{z_s F} |i_s(E_{mix}^{m+1})| c_s^{m+1}, \quad -D_k \frac{\partial c_k^{m+1}}{\partial \mathbf{n}} = \frac{1}{z_k F} |i_k(E_{mix}^{m+1})| c_k^{m+1}, \quad -D_g \frac{\partial c_g^{m+1}}{\partial \mathbf{n}} = \beta D_s \frac{\partial c_s^{m+1}}{\partial \mathbf{n}} \quad (\text{B.9})$$

where

$$\begin{aligned} i_s(E_{mix}^{m+1}) &= L_s \left( \exp \left( \frac{\alpha_s z_s F (E_{mix}^{m+1} - E_s)}{R\theta} \right) - \exp \left( \frac{-\beta_s z_s F (E_{mix}^{m+1} - E_s)}{R\theta} \right) \right), \\ i_k(E_{mix}^{m+1}) &= L_k \left( \exp \left( \frac{\alpha_k z_k F (E_{mix}^{m+1} - E_k)}{R\theta} \right) - \exp \left( \frac{-\beta_k z_k F (E_{mix}^{m+1} - E_k)}{R\theta} \right) \right), \\ i_s(E_{mix}^{m+1}) c_s^{m+1} + i_k(E_{mix}^{m+1}) c_k^{m+1} &= 0. \end{aligned}$$

In the following context, we define  $i_s^{m+1} := |i_s(E_{mix}^{m+1})|$ ,  $i_k^{m+1} := |i_k(E_{mix}^{m+1})|$ .

Let us begin with the upper bound and the lower bound of  $r_l$ .

**Lemma B.2.1** Assume that  $0 < \epsilon < r_l^j < 1$ ,  $c_g^j \geq 0$ ,  $c_g^j \in H^1(\Omega) \cap L^\infty(\Omega)$  and  $r_l^j \in H^1(\Omega)$  for all integer  $0 \leq j \leq m$ , then

$$(i) \quad 0 < \frac{\epsilon}{1 + K\delta t/\rho_g} < r_l^{m+1} < 1.$$

$$(ii) \quad \frac{1}{r_l^{m+1}} \in L^\infty(\Omega)$$

$$(iii) \quad r_l^{m+1} \in H^1(\Omega)$$

*Proof.* By the first equation of (B.8), we have

$$\left( 1 + \frac{K\delta t}{\rho_g} c_g^m \right) r_l^{m+1} = r_l^m. \quad (\text{B.10})$$

By the assumption  $c_g^m \geq 0$ , we have

$$r_l^{m+1} \leq 1, \quad \frac{\epsilon}{1 + K\delta t/\rho_l} < r_l^{m+1}.$$

This proves (i). Since  $1 < \frac{1}{r_l^{m+1}} < \frac{1 + K\delta t/\rho_l}{\epsilon}$ , we have proved (ii).

Taking the derivative with respect to  $x_i$  in (B.10), we have

$$\left( 1 + \frac{K\delta t}{\rho_g} c_g^m \right) \partial_{x_i} r_l^{m+1} = -\frac{K\delta t}{\rho_g} r_l^{m+1} \partial_{x_i} c_g^m + \partial_{x_i} r_l^m. \quad (\text{B.11})$$

Since  $\partial_{x_i} r_l^m$ ,  $r_l^{m+1} \partial_{x_i} c_g^m$  are bounded in  $L^2(\Omega)$ , we can conclude that  $\partial_{x_i} r_l^{m+1}$  is bounded in  $L^2(\Omega)$ . This proves (iii). Q.E.D.

The weak formulation regarding the system (B.8) except its first equation can be expressed as:

**Problem  $(\bar{P}_c)$ :**

Let  $0 < r_l^m, r_l^{m+1} \leq 1$ ,  $r_l^m, r_l^{m+1} \in H^1(\Omega)$ ,  $0 < c_s^m, c_k^m \leq 1$ ,  $c_g^m \geq 0$ ,  $c_s^m, c_k^m, c_g^m \in H_{r_l^m}^1(\Omega)$ . Find



$c_s^{m+1}, c_k^{m+1}, c_g^{m+1} \in H_{r_l^{m+1}}^1(\Omega)$  and  $E_{mix}^{m+1} \in L^2(S)$  such that

$$\frac{1}{\delta t}(c_s^{m+1}, w_s)_{r_l^{m+1}} + D_s(\nabla c_s^{m+1}, \nabla w_s)_{r_l^{m+1}} + \frac{1}{z_s F}(r_l^{m+1} i_s^{m+1} c_s^{m+1}, w_s)_{L^2(S)} = \frac{1}{\delta t}(c_s^m, w_s)_{r_l^{m+1}} \quad (\text{B.12})$$

$$\frac{1}{\delta t}(c_k^{m+1}, w_k)_{r_l^{m+1}} + D_k(\nabla c_k^{m+1}, \nabla w_k)_{r_l^{m+1}} + \frac{1}{z_k F}(r_l^{m+1} i_k^{m+1} c_k^{m+1}, w_k)_{L^2(S)} = \frac{1}{\delta t}(c_k^m, w_k)_{r_l^{m+1}} \quad (\text{B.13})$$

$$\begin{aligned} & \frac{1}{\delta t}(c_g^{m+1}, w_g)_{r_l^{m+1}} + D_g(\nabla c_g^{m+1}, \nabla w_g)_{r_l^{m+1}} - \frac{\beta}{z_s F}(r_l^{m+1} i_s^{m+1} c_s^{m+1}, w_g)_{L^2(S)} \\ & + \left( \frac{M_g K_g}{\rho_l} c_g^{m+1}, w_g \right)_{r_l^{m+1}} = \frac{1}{\delta t}(c_g^m, w_g)_{r_l^{m+1}} \end{aligned} \quad (\text{B.14})$$

$$(i_s(E_{mix}^{m+1}) + i_k(E_{mix}^{m+1}), w)_{L^2(S)} = 0 \quad (\text{B.15})$$

for all  $w_s, w_k, w_g \in H^1(\Omega)$  and  $w \in L^2(S)$ .

### B.3 Existence of the time-discrete problem

**Proposition B.3.1** If  $E_{mix}^{m+1} \in B := \{w \in L^2(S) \mid E_k \leq w \leq E_s \text{ a.e.}\}$  is given, There exist unique solutions  $(c_s^{m+1}, c_k^{m+1}, c_g^{m+1})$  for Problem  $(\widetilde{P}_c)$ .

*Proof.* The existence and uniqueness for  $c_s^{m+1}, c_k^{m+1}$  and  $c_g^{m+1}$  can be guaranteed by a classic theory since (B.12)-(B.14) are linear.

If  $E_{mix}^{m+1}$  is given, we can further obtain the positivity for  $c_s^{m+1}, c_k^{m+1}$  and  $c_g^{m+1}$ .

**Proposition B.3.2** Let  $E_{mix}^{m+1} \in B$ , if  $c_s^m, c_k^m, c_g^m \geq 0$  a.e., then  $c_s^{m+1}, c_k^{m+1}, c_g^{m+1} \geq 0$  a.e..

*Proof.* Similar to the proof of Proposition 2.4.2, the nonnegativity of  $c_s^{m+1}, c_k^{m+1}, c_g^{m+1}$  can be guaranteed by letting  $w_s = (c_s^{m+1})^-, w_k = (c_k^{m+1})^-, w_g = (c_g^{m+1})^-$ . Q.E.D.

**Proposition B.3.3** Let  $E_{mix}^{m+1} \in B$ ,  $0 < c_s^j, c_k^j \leq 1$ ,  $E_{mix}^j \in B$ , for all  $0 \leq j \leq m$ . Furthermore, we assume that  $0 \leq c_g^0 < M$  for some positive constant  $M$ , we have

$$c_s^{m+1}, c_k^{m+1} \leq 1 \quad (\text{B.16})$$

and there exists a positive constant  $C$  depending only on  $\Omega, D_g, T$ , such that

$$c_g^{m+1} \leq C, \quad (\text{B.17})$$

*Proof.* To obtain (B.16), we can take  $w_s = (w_s - 1)^+$  and  $w_k = (w_k - 1)^+$  in (B.12) and (B.13), respectively. The proof of (B.17) is extremely technical which can be referred to Lemma II 5.7 and Theorem II 6.2 in [70]. Q.E.D.

If the value of mixed potential  $E_{mix}^{m+1}$  is restricted in  $[E_k, E_s]$ , the  $L^\infty$  norms of  $i_s^{m+1}, i_k^{m+1}$  are uniformly bounded in terms of  $E_{mix}^{m+1}$ , respectively. By Thoerem 4 in [73], we have the following:

**Lemma B.3.1 (Strong positivity for  $c_s^{m+1}$  and  $c_k^{m+1}$ )** Let  $c_s^m, c_k^m \geq 0$ ,  $E_{mix}^{m+1} \in B$ . Assuming further that there are constant  $\eta_s^m, \eta_k^m > 0$  such that  $c_s^m \geq \eta_s^m$  and  $c_k^m \geq \eta_k^m$  a.e., there are constants  $\eta_s^{m+1}, \eta_k^{m+1} > 0$  such that  $c_s^{m+1} \geq \eta_s^{m+1}$ , and  $c_k^{m+1} \geq \eta_k^{m+1}$  a.e.. Moreover,  $c_s^{m+1}$  and  $c_k^{m+1}$  are Hölder continuous in  $\bar{\Omega}$  for some exponent  $0 < \alpha < 1$ .

**Corollary B.3.1** Assuming that  $\|c_s^j\|_{L^\infty(\Omega)}$  is uniformly bounded for all  $0 \leq j \leq N$ , there is a generic constant  $C > 0$  such that

$$\left\| \frac{r_l^{j+1} - r_l^j}{\delta t} \right\|_{L^\infty(\Omega)} \leq C \quad (\text{B.18})$$

for all  $0 \leq j \leq N$ .

To show the existence for the full problem  $(\widetilde{P}_c)$ , the Browder fixed point theorem can be applied:

**Theorem B.3.1 (Schauder fixed point theorem)** Let  $K$  be a nonempty closed convex set in a Banach space. If a function  $f : K \rightarrow K$  is compact, then  $f$  has a fixed point.

**Lemma B.3.2**  $B := \{w \in L^2(S) \mid E_k \leq w \leq E_s \text{ a.e.}\}$  is a closed bounded convex subset in  $L^2(S)$ .

*Proof.* Since  $S$  is of finite measure, it is obvious that  $B$  is bounded. Let  $\theta \in (0, 1)$ , for  $w_1, w_2 \in B$  we have  $\theta E_k \leq \theta w_1 \leq \theta E_s$  and  $(1 - \theta)E_k \leq (1 - \theta)w_2 \leq (1 - \theta)E_s$ . Therefore  $E_k \leq \theta w_1 + (1 - \theta)w_2 \leq E_s$ . This implies that  $B$  is convex. Finally, let  $x$  be a limit point of  $B$ , there exists a sequence  $\{x_n\}_{n=1}^\infty \subset B$  such that

$$\|x_n - x\|_{L^2(S)} \rightarrow 0 \quad \text{as } n \rightarrow \infty$$

This shows that  $E_k \leq x \leq E_s$  almost everywhere on  $S$ . This completes the proof. Q.E.D.

We define the space  $W_\eta := \{w \in H_{r_l^{m+1}}^1(\Omega) \mid \eta \leq w \leq 1 \text{ a.e.}\}$ . Given Lemma B.3.1, we define  $\eta_s^{m+1}, \eta_k^{m+1}$  to be the essential infimum of  $c_s^{m+1}, c_k^{m+1}$ , respectively. Let us define the mapping  $\Gamma_1 : B \rightarrow \mathbf{H} := W_{\eta_s^{m+1}} \times W_{\eta_k^{m+1}}$  such that  $\Gamma_1(E)$  is the set of solutions to  $(\widetilde{P}_{c_s})$ , and  $(\widetilde{P}_{c_k})$ , respectively, when letting  $E_{mix}^{m+1} = E$ .

**Lemma B.3.3**  $\Gamma_1$  is a bounded operator.

*Proof.* Let  $w_s = c_s^{m+1}$  in (B.12), we have

$$\begin{aligned} & \frac{1}{\delta t} \|c_s^{m+1}\|_{r_l^{m+1}}^2 + D_s \|\nabla c_s^{m+1}\|_{r_l^{m+1}}^2 + (r_l^{m+1} i_s^{m+1} c_s^{m+1}, c_s^{m+1})_{L^2(S)} \\ &= \frac{1}{\delta t} (c_s^m, c_s^{m+1})_{r_l^{m+1}} \\ &\leq \frac{1}{\delta t} \|c_s^m\|_{r_l^m} \|c_s^{m+1}\|_{r_l^{m+1}} \\ &\leq \|c_s^m\|_{r_l^m} \left( \|c_s^{m+1}\|_{r_l^{m+1}}^2 + D_s \delta t \|\nabla c_s^{m+1}\|_{r_l^{m+1}}^2 \right)^{\frac{1}{2}} \end{aligned} \quad (\text{B.19})$$

This shows that the bound for  $c_s^{m+1}$  is independent of  $i_s$ . By the same argument, we can show that  $c_k^{m+1}$  is uniformly bounded as well. We recall that the element in  $B$  has a minimal norm  $\|E_s\|_{L^2(S)}$ . There must exists a sufficiently large constant  $M > 0$  such that

$$\begin{aligned} & \delta t \left( \frac{K}{\rho l} \|c_g^{m+1}\|_{L^\infty(\Omega)} + \frac{1}{\delta t} \left( \left\| \frac{1}{r_l^{m+1}} \right\|_{L^\infty(\Omega)} \|r_l^m\|_{L^\infty(\Omega)} \right)^{\frac{1}{2}} \|c_s^m\|_{r_l^m} \right) \\ &\leq M \|E_s\|_{L^2(S)} \leq M \|E\|_{L^2(S)} \end{aligned} \quad (\text{B.20})$$

for all  $E \in B$ . Q.E.D.

By Corollary 7.3 in [11], we have:

**Lemma B.3.4** The trace operator  $T : \mathbf{H} \rightarrow L^2(S) \times L^2(S)$  is compact.

Now we define the operator  $\Gamma_2 : T(\mathbf{H}) \rightarrow L^2(S)$  by

$$\Gamma_2(c_s, c_k) = \frac{c_s}{c_k}, \quad (c_s, c_k) \in \mathbf{H}.$$

**Lemma B.3.5**  $\Gamma_2$  is a bounded operator.

*Proof.* Let  $(c_s, c_k) \in T(\mathbf{H})$ , we have, pointwisely

$$\left| \frac{c_s}{c_k} \right| \leq \frac{1}{\eta_k^{m+1}} |c_s|. \quad (\text{B.21})$$

Therefore,

$$\begin{aligned} \left\| \frac{c_s}{c_k} \right\|_{L^2(S)}^2 &\leq \frac{1}{(\eta_k^{m+1})^2} \int_S |c_s|^2 d\sigma \leq \frac{1}{(\eta_k^{m+1})^2} \int_S |c_s|^2 + |c_k|^2 d\sigma \\ &= \frac{1}{(\eta_k^{m+1})^2} (\|c_s\|_{L^2(S)}^2 + \|c_k\|_{L^2(S)}^2) \end{aligned} \quad (\text{B.22})$$

This completes the proof. Q.E.D.

Finally, we define  $\Gamma_3 : \Gamma_2(T(\mathbf{H})) \rightarrow B$  by

$$\Gamma_3 : \zeta \mapsto E,$$

where  $E$  satisfying  $i_s(E)\zeta + i_k(E) = 0$  pointwisely.

**Lemma B.3.6**  $\Gamma_3$  is a bounded operator.

*Proof.* We write  $\zeta = \zeta(E)$ , we have  $\zeta(E) = -\frac{i_k(E)}{i_s(E)}$ . Observing that  $i_k(E) > 0$  and  $i_s(E) < 0$  for  $E \in (E_k, E_s)$ , since  $i_k(E)$  is strictly increasing and  $-i_s(E)$  is strictly decreasing, we have  $\zeta(E)$  is strictly increasing. Therefore,  $\Gamma_3$  is the inverse of  $\zeta$ . Since  $i_k(E)$  and  $i_s(E)$  are linear combinations of exponential function of  $E$ , respectively, and  $i_s(E) < 0$  for  $E \in (E_k, E_s)$ ,  $\zeta(E)$  is differentiable in  $(E_k, E_s)$ . Therefore, we have

$$\zeta'(E) = \frac{1}{\Gamma_3'(\zeta)}.$$

For any element  $c = (c_s, c_k)$  in  $T(\mathbf{H})$ , we always have

$$\min(\eta_k^{m+1}, \eta_s^{m+1}) \leq \frac{c_k}{c_s} \leq \frac{1}{\min(\eta_k^{m+1}, \eta_s^{m+1})}.$$

Now we are going to seek the upper bound of  $\Gamma_3'(\zeta)$  for

$\zeta \in [\min(\eta_k^{m+1}, \eta_s^{m+1}), \frac{1}{\min(\eta_k^{m+1}, \eta_s^{m+1})}]$ . By the strict monotonicity of  $\zeta$ , there are constants  $m$  and  $M$  such that  $E_k < m < M < E_s$  so that

$$\Gamma_3([\min(\eta_k^{m+1}, \eta_s^{m+1}), \frac{1}{\min(\eta_k^{m+1}, \eta_s^{m+1})}]) \subset [m, M].$$

Let  $\alpha_1 = \frac{\alpha_s z_s F}{R\theta}$ ,  $\alpha_2 = \frac{\alpha_k z_k F}{R\theta}$ ,  $\beta_1 = \frac{\beta_s z_s F}{R\theta}$ ,  $\beta_2 = \frac{\beta_k z_k F}{R\theta}$ , we have

$$\begin{aligned} \zeta'(E) &= -\frac{L_k}{L_s} \frac{1}{(e^{\alpha_1(E-E_s)} - e^{-\beta_1(E-E_s)})^2} [(e^{\alpha_1(E-E_s)} - e^{-\beta_1(E-E_s)})(\alpha_2 e^{\alpha_2(E-E_k)} + \beta_2 e^{\beta_2(E-E_k)}) \\ &\quad - (e^{\alpha_2(E-E_k)} - e^{\beta_2(E-E_k)})(\alpha_2 e^{\alpha_2(E-E_k)} + \beta_2 e^{\beta_2(E-E_k)})] \end{aligned} \quad (\text{B.23})$$

For  $m \leq E \leq M$ , we have

$$\zeta'(E) \geq \frac{L_k}{L_s} \frac{(e^{-\beta_1(M-E_s)} - e^{\alpha_1(M-E_s)})(\alpha_2 e^{\alpha_2(m-E_k)} + \beta_2 e^{-\beta_2(m-E_k)})}{(e^{\alpha_1(m-E_s)} - e^{-\beta_1(m-E_s)})^2} \quad (\text{B.24})$$

Therefore, there is a constant  $\widetilde{M}$  such that  $|\Gamma'_3(\zeta)| \leq \widetilde{M}$  for all  $\zeta \in [\min(\eta_k^{m+1}, \eta_s^{m+1}), \frac{1}{\min(\eta_k^{m+1}, \eta_s^{m+1})}]$ . Finally we have

$$|\Gamma_3(\zeta)| \leq \min(\eta_k^{m+1}, \eta_s^{m+1}) + \widetilde{M}|\zeta| \leq (\widetilde{M} + 1)|\zeta|.$$

The proof can be completed by integrating the square of the above inequality. Q.E.D.

**Proposition B.3.4** The operator  $\Gamma = \Gamma_3 \circ \Gamma_2 \circ T \circ \Gamma_1 : B \rightarrow B$  has a fixed point.

*Proof.* Since  $B$  is convex and closed by Lemma B.3.2 and the composition of bounded operator with compact operator (also their commutation) is compact, the existence of the fixed point can be proved by the Schauder fixed point theorem with Lemmas B.3.3, B.3.4, B.3.5, B.3.6. Q.E.D.

Now, we have the theorem

**Theorem B.3.2** If  $\delta t > 0$  is sufficiently small, the system Problems  $(\widetilde{P}_c)$  is well-posed.

*Proof.* It remains to prove the uniqueness of the system. Assuming that  $(c_{s1}, c_{k1}, E_1), (c_{s2}, c_{k2}, E_2) \in W_{\eta_s^{m+1}} \times W_{\eta_k^{m+1}} \times B$  are two different solutions. If  $E_1 = E_2$ , then we must have  $c_{s1} = c_{s2}$  and  $c_{k1} = c_{k2}$  by the uniqueness of Problems  $(\widetilde{P}_c)$ . Therefore, we may assume that  $E_1 \neq E_2$  for all  $\delta t > 0$ . By (B.12) and (B.13), we have

$$\begin{aligned} &(c_{s1} - c_{s2}, w_s)_{r_l^{m+1}} + \delta t D_s(\nabla(c_{s1} - c_{s2}), w_s)_{r_l^{m+1}} \\ &+ \frac{1}{z_s F} (r_l^{m+1}(|i_s(E_1)|c_{s1} - |i_s(E_2)|c_{s2}), w_s)_{L^2(S)} \\ &+ (c_{k1} - c_{k2}, w_k)_{r_l^{m+1}} + \delta t D_k(\nabla(c_{k1} - c_{k2}), w_k)_{r_l^{m+1}} \\ &+ \frac{1}{z_k F} (r_l^{m+1}(|i_k(E_1)|c_{k1} - |i_k(E_2)|c_{k2}), w_k)_{L^2(S)} \\ &= 0. \end{aligned} \quad (\text{B.25})$$

To estimate the boundary term, we observe pointwisely:

$$|i_s(E_1)|c_{s1} - |i_s(E_2)|c_{s2} = |i_s(E_1)|(c_{s1} - c_{s2}) - c_{s2}(|i_s(E_1)| - |i_s(E_2)|). \quad (\text{B.26})$$

Using notations in Lemma B.3.6, we have, pointwisely

$$\begin{aligned}
| |i_s(E_1)| - |i_s(E_2)| | &= L_s \left| (e^{\alpha_1(E_1-E_s)} - e^{-\beta_1(E_1-E_s)}) - (e^{\alpha_1(E_2-E_s)} - e^{-\beta_1(E_2-E_s)}) \right| \\
&\leq L_s \left( \alpha_1 + \beta_1 e^{\beta_1(E_s-E_k)} \right) |E_1 - E_2| \\
&\leq L_s \left( \alpha_1 + \beta_1 e^{\beta_1(E_s-E_k)} \right) \widetilde{M} \left| \frac{c_{s1}}{c_{k1}} - \frac{c_{s2}}{c_{k2}} \right| \\
&\leq L_s \left( \alpha_1 + \beta_1 e^{\beta_1(E_s-E_k)} \right) \frac{\widetilde{M}}{(\eta_k^{m+1})^2} (|c_{s1} - c_{s2}| + |c_{k1} - c_{k2}|)
\end{aligned} \tag{B.27}$$

Similarly, we have

$$|i_s(E_1)| - |i_s(E_2)| \leq L_k (\alpha_2 e^{\alpha_2(E_s-E_k)} + \beta_2) \frac{\widetilde{M}}{(\eta_k^{m+1})^2} (|c_{s1} - c_{s2}| + |c_{k1} - c_{k2}|). \tag{B.28}$$

Now letting  $w_s = c_{s1} - c_{s2}$  and  $w_k = c_{k1} - c_{k2}$  in (B.25) and by (B.26)-(B.28) with Hölder inequality, there is a generic constant  $C$  such that

$$\begin{aligned}
&\|c_{s1} - c_{s2}\|_{r_l^{m+1}}^2 + \|c_{k1} - c_{k2}\|_{r_l^{m+1}}^2 + \delta t D_s \|\nabla(c_{s1} - c_{s2})\|_{r_l^{m+1}}^2 + \delta t D_k \|\nabla(c_{k1} - c_{k2})\|_{r_l^{m+1}}^2 \\
&\leq C \delta t (\|c_{s1} - c_{s2}\|_{L^2(S)}^2 + \|c_{k1} - c_{k2}\|_{L^2(S)}^2)
\end{aligned} \tag{B.29}$$

Since  $\|\frac{1}{r_l}\|_{L^\infty(0,T;L^\infty(\Omega))}$  is bounded, we also have

$$\begin{aligned}
&\|c_{s1} - c_{s2}\|_0^2 + \|c_{k1} - c_{k2}\|_0^2 + \delta t D_s \|\nabla(c_{s1} - c_{s2})\|_0^2 + \delta t D_k \|\nabla(c_{k1} - c_{k2})\|_0^2 \\
&\leq C \delta t (\|c_{s1} - c_{s2}\|_{L^2(S)}^2 + \|c_{k1} - c_{k2}\|_{L^2(S)}^2)
\end{aligned} \tag{B.30}$$

for some constant  $C > 0$ . Applying the trace inequality, there is a constant  $C_1 > 0$  such that

$$\begin{aligned}
&\|c_{s1} - c_{s2}\|_{L^2(S)}^2 \leq C_1 \|c_{s1} - c_{s2}\|_0 \|c_{s1} - c_{s2}\|_1 \\
&\leq \frac{C_1}{2\epsilon_1} \|c_{s1} - c_{s2}\|_0^2 + \frac{C_1 \epsilon_1}{2} \|c_{s1} - c_{s2}\|_1^2 = \left( \frac{C_1}{2\epsilon_1} + \frac{C_1 \epsilon_1}{2} \right) \|c_{s1} - c_{s2}\|_0^2 + \frac{C_1 \epsilon_1}{2} \|\nabla(c_{s1} - c_{s2})\|_0^2
\end{aligned} \tag{B.31}$$

for all  $\epsilon_1 > 0$ . Similarly, there is a constant  $C_2 > 0$  such that

$$\|c_{k1} - c_{k2}\|_{L^2(S)}^2 \leq \left( \frac{C_2}{2\epsilon_2} + \frac{C_2 \epsilon_2}{2} \right) \|c_{k1} - c_{k2}\|_0^2 + \frac{C_2 \epsilon_2}{2} \|\nabla(c_{k1} - c_{k2})\|_0^2 \tag{B.32}$$

for all  $\epsilon_2 > 0$ . Choosing  $\epsilon_1 = \frac{2D_s}{C_1}$ ,  $\epsilon_2 = \frac{2D_k}{C_2}$  and

$$\delta t \leq \min \left( \frac{1}{2 \left( \frac{C_1^2}{4D_s} + D_s \right)}, \frac{1}{2 \left( \frac{C_2^2}{4D_k} + D_k \right)} \right),$$

we have

$$\frac{1}{2} \|c_{s1} - c_{s2}\|_0^2 + \frac{1}{2} \|c_{k1} - c_{k2}\|_0^2 \leq 0. \tag{B.33}$$

This implies that  $c_{s1} = c_{s2}$  and  $c_{k1} = c_{k2}$ . Since  $c_{s1}, c_{s2}, c_{k1}, c_{k2} \in C(\bar{\Omega})$ , the unique solvability for (B.15) implies that  $E_1 = E_2$  on  $S$ . This leads to the contradiction. Q.E.D.

**Remark B.3.1** In the above theorem, the choice of  $\delta t$  is independent of the data of the previous step  $(c_s^m, c_k^m, E_{mix}^m)$ . Therefore, the unique solution for time-discrete problem at time  $t = T$  can be reached in finite steps.

## B.4 Stability analysis

Since the uniform bounds independent of  $E_{mix}^{m+1}$  have been found for  $L^\infty$  boundedness of  $c_s^m$  and  $c_k^m$ ,  $m = 0, \dots, N$ . Now we provide some results of stability:

**Lemma B.4.1** Let  $0 \leq c_j^0 \leq 1$ ,  $c_j^0 \in H^1(\Omega)$  for  $j = s, k, g$ , and  $E_{mix}^0 \in B$ . There are generic constants  $C > 0$  such that

$$\delta t \sum_{j=s,k,g} \sum_{m=0}^{N-1} \|\nabla c_j^{m+1}\|_{r_l^{m+1}}^2 \leq C \quad (\text{B.34})$$

*Proof.* Letting  $w_s = c_s^{m+1}$  in (B.12), we have

$$\begin{aligned} & \|c_s^{m+1}\|_{r_l^{m+1}}^2 + \delta t D_s \|\nabla c_s^{m+1}\|_{r_l^{m+1}}^2 + \delta t (r_l^{m+1} i_s^{m+1} c_s^{m+1}, c_s^{m+1})_{L^2(S)} \\ &= (c_s^m, c_s^{m+1})_{r_l^{m+1}} \leq \|c_s^m\|_{r_l^m} \|c_s^{m+1}\|_{r_l^{m+1}} \\ &\leq \frac{1}{2} \|c_s^m\|_{r_l^m}^2 + \frac{1}{2} \|c_s^{m+1}\|_{r_l^{m+1}}^2. \end{aligned} \quad (\text{B.35})$$

Similarly, letting  $w_k = c_k^{m+1}$  in (B.13), we have

$$\begin{aligned} & \|c_k^{m+1}\|_{r_l^{m+1}}^2 + \delta t D_k \|\nabla c_k^{m+1}\|_{r_l^{m+1}}^2 + \delta t (r_l^{m+1} i_k^{m+1} c_k^{m+1}, c_k^{m+1})_{L^2(S)} \\ &\leq \frac{1}{2} \|c_k^m\|_{r_l^m}^2 + \frac{1}{2} \|c_k^{m+1}\|_{r_l^{m+1}}^2. \end{aligned} \quad (\text{B.36})$$

Once more, letting  $w_g = c_g^{m+1}$  in (B.14), we have

$$\begin{aligned} & \|c_g^{m+1}\|_{r_l^{m+1}}^2 + \delta t D_g \|\nabla c_g^{m+1}\|_{r_l^{m+1}}^2 + \delta t \frac{M_g K_g}{\rho_l} \|c_g^{m+1}\|_0^2 \\ &= (c_g^m, c_g^{m+1})_{r_l^{m+1}} + \beta \delta t (r_l^{m+1} i_s^{m+1} c_s^{m+1}, c_g^{m+1})_{L^2(S)} \\ &\leq \frac{1}{2} \|c_g^m\|_{r_l^m}^2 + \frac{1}{2} \|c_g^{m+1}\|_{r_l^{m+1}}^2 + \beta \delta t (r_l^{m+1} i_s^{m+1} c_s^{m+1}, c_g^{m+1}) \\ &\leq \frac{1}{2} \|c_g^m\|_{r_l^m}^2 + \frac{1}{2} \|c_g^{m+1}\|_{r_l^{m+1}}^2 + \beta \delta t \|i_s\|_{L^2(S)} \|c_g\|_{L^2(S)} \\ &\leq \frac{1}{2} \|c_g^m\|_{r_l^m}^2 + \frac{1}{2} \|c_g^{m+1}\|_{r_l^{m+1}}^2 + \beta \delta t \left( \frac{1}{2\epsilon} \|i_s\|_{L^2(S)}^2 + \frac{\epsilon}{2} \|c_g\|_{L^2(S)}^2 \right) \\ &\leq \frac{1}{2} \|c_g^m\|_{r_l^m}^2 + \frac{1}{2} \|c_g^{m+1}\|_{r_l^{m+1}}^2 + C \delta t \left( \frac{1}{2\epsilon} \|i_s\|_{L^2(S)}^2 + \frac{\epsilon}{2} \|c_g\|_1^2 \right) \end{aligned} \quad (\text{B.37})$$

Therefore, we have

$$(1 + \delta t \frac{M_g K_g}{\rho_l} - C \epsilon \delta t) \|c_g^{m+1}\|_{r_l^{m+1}}^2 + \delta t (2D_g - C \epsilon) \|\nabla c_g\|_{r_l^{m+1}}^2 \leq \frac{C \delta t}{\epsilon} \|i_s\|_{L^2(S)}^2 + \|c_g^m\|_{r_l^m}^2 \quad (\text{B.38})$$

Taking  $\epsilon = \frac{D_g}{C}$  sufficiently small so that and using the fact that  $c_g^{m+1}$  has a uniform  $L^\infty$  bound. We can conclude that there exists a generic constant  $C > 0$  such that

$$\|\nabla c_g^{m+1}\|_0^2 \leq C \quad (\text{B.39})$$

Collecting (B.35), (B.36), and (B.39) and taking the summation from 0 to  $\frac{T}{\delta t} - 1$ , the proof is completed. Q.E.D.

Since  $\|\frac{1}{r_l^{m+1}}\|_{L^\infty(\Omega)}$  is bounded for all  $m = 0, \dots, N$ , we have

**Corollary B.4.1** There are generic constants  $C > 0$  such that

$$\delta t \sum_{j=s,k,g} \sum_{m=0}^{N-1} \|\nabla c_j^{m+1}\|_0^2 \leq C \quad (\text{B.40})$$

**Lemma B.4.2** There are generic constants  $C > 0$  such that

$$\sum_{j=s,k,g} \sum_{m=0}^{N-1} \|r_l^{m+1}(c_j^{m+1} - c_j^m)\|_0^2 \leq C. \quad (\text{B.41})$$

*Proof.* The proof is almost identical to Lemma B.4.1 with the fact that

$$\begin{aligned} & (r_l^{m+1}c_j^{m+1} - c_j^m, c_j^{m+1}) \\ &= \frac{1}{2}\|c_j^{m+1}\|_{r_l^{m+1}}^2 + \frac{1}{2}\|c_j^m - c_j^{m+1}\|_{r_l^{m+1}}^2 - \frac{1}{2}\|c_j^m\|_{r_l^{m+1}}^2 \\ &\leq \frac{1}{2}\|c_j^{m+1}\|_{r_l^{m+1}}^2 + \frac{1}{2}\|c_j^m - c_j^{m+1}\|_{r_l^{m+1}}^2 - \frac{1}{2}\|c_j^m\|_{r_l^m}^2 \end{aligned} \quad (\text{B.42})$$

Q.E.D.

**Lemma B.4.3** There are generic constants  $C > 0$  such that

$$\delta t \sum_{j=s,k,g} \sum_{m=0}^{N-1} \left\| \frac{r_l^{m+1}(c_j^{m+1} - c_j^m)}{\delta t} \right\|_{(H^1(\Omega))'}^2 \leq C \quad (\text{B.43})$$

*Proof.* We only look for the boundedness of  $c_s$  and the case is similar for  $k$  and  $dis$ . By definition

$$\left\| \frac{r_l^{m+1}(c_s^{m+1} - c_s^m)}{\delta t} \right\|_{(H^1(\Omega))'} = \sup_{w_s \in H^1(\Omega)} \left\langle \frac{r_l^{m+1}(c_s^{m+1} - c_s^m)}{\delta t}, w_s \right\rangle \quad (\text{B.44})$$

By (B.12), with  $w = \frac{w_s}{\|w_s\|_1} \in H^1(\Omega)$ ,

$$\begin{aligned} & \left\| \frac{r_l^{m+1}(c_s^{m+1} - c_s^m)}{\delta t} \right\|_{(H^1(\Omega))'} \\ &= \sup_{w \in H^1(\Omega), \|w\|_1=1} \left\{ -D_s(\nabla c_s^{m+1}, \nabla w)_{r_l^{m+1}} - \frac{1}{z_s F} (r_l^{m+1} |i_s^{m+1}| c_s^{m+1}, w)_{L^2(S)} \right\} \end{aligned} \quad (\text{B.45})$$

We estimate all terms on the right hand side of (B.45):

$$\begin{aligned} -D_s(\nabla c_s^{m+1}, \nabla w)_{r_l^{m+1}} &\leq D_s \|\nabla c_s^{m+1}\|_{r_l^{m+1}} \|\nabla w\|_{r_l^{m+1}} \\ &\leq D_s \|\nabla c_s^{m+1}\|_{r_l^{m+1}} \|\nabla w\| \leq D_s \|\nabla c_s^{m+1}\|_{r_l^{m+1}} \|w\|_1 \leq D_s \|\nabla c_s^{m+1}\|_{r_l^{m+1}}, \end{aligned} \quad (\text{B.46})$$

$$\begin{aligned} -\frac{1}{z_s F} (r_l^{m+1} |i_s^{m+1}| c_s^{m+1}, w)_{L^2(S)} &\leq \frac{1}{z_s F} |i_s(E_k)| \|c_s^{m+1}\|_{L^2(S)} \|w\|_{L^2(S)} \\ &\leq C \|c_s^{m+1}\|_1 \|w\|_1 = C \|c_s^{m+1}\|_1, \end{aligned} \quad (\text{B.47})$$

Collecting (B.46)-(B.47) and multiplying by  $\delta t$  gives

$$\delta t \left\| \frac{r_l^{m+1} (c_s^{m+1} - c_s^m)}{\delta t} \right\|_{(H^1(\Omega))'}^2 \leq C \delta t (\|c_s^m\|_1^2 + \|c_s^{m+1}\|_1^2). \quad (\text{B.48})$$

Taking the summation from 0 to  $N-1$  and the boundedness given by Corollary B.4.1 and Lemma B.3.3, we have the desired estimate. Q.E.D.

**Corollary B.4.2** There are generic constants  $C > 0$  such that

$$\delta t \sum_{j=s,k,g} \sum_{m=0}^{N-1} \left\| \frac{c_j^{m+1} - c_j^m}{\delta t} \right\|_{(H^1(\Omega))'}^2 \leq C \quad (\text{B.49})$$

*Proof.* This is the direct result from Lemma B.4.3 and the fact that  $r_l^{m+1}$  is bounded in  $L^\infty(\Omega)$ . Q.E.D.

**Corollary B.4.3** There are generic constants  $C > 0$  such that

$$\delta t \sum_{j=s,k,g} \sum_{m=0}^{N-1} \left\| \frac{r_j^{m+1} c_j^{m+1} - r_j^m c_j^m}{\delta t} \right\|_{(H^1(\Omega))'}^2 \leq C \quad (\text{B.50})$$

*Proof.* By the relation

$$r_l^{m+1} c_j^{m+1} - r_l^m c_j^m = r_l^{m+1} (c_j^{m+1} - c_j^{m+1}) + c_s^m (r_l^{m+1} - r_l^m), \quad 0 \leq m \leq M-1,$$

the desired result can be obtained by collecting Lemma B.4.3, Corollary B.4.2 and the  $L^\infty$  boundedness of  $r_l^m$  for all  $0 \leq m \leq N$ . Q.E.D.

**Lemma B.4.4** Assuming that  $r_l^j \in H^1(\Omega)$ ,  $0 < r_l^j \leq 1$ ,  $c_g^j \in H^1(\Omega) \cap L^\infty(\Omega)$ ,  $c_g^j \geq 0$  for all  $0 \leq j \leq m \leq N$ , then we have the estimate

$$\|\nabla r_l^k\|_0^2 \leq \exp\left(\frac{K_g T}{\rho_g}\right) (\|\nabla r_l^0\|_0^2 + \frac{K_g \delta t}{\rho_g} \sum_{m=0}^{N-1} \|\nabla c_g^m\|_0^2). \quad (\text{B.51})$$

*Proof.* Multiplying (C.11) with  $\partial_{x_i} r_l^{m+1}$  and integrating the both sides with respect to  $\Omega$ , we



have

$$\begin{aligned}
& \int_{\Omega} (1 + \frac{K\delta t}{\rho_g} c_g^m) |\nabla r_l^{m+1}|^2 dx = -\frac{K\delta t}{\rho_g} \int_{\Omega} \nabla c_g^m \cdot \nabla r_l^{m+1} dx + \int_{\Omega} \nabla r_l^m \cdot \nabla r_l^{m+1} dx \\
& \leq \frac{K\delta t}{\rho_g} \|\nabla c_g^m\|_0 \|\nabla r_l^{m+1}\|_0 + \|\nabla r_l^m\|_0 \|\nabla r_l^{m+1}\|_0 \\
& \leq \frac{1}{2} \|\nabla r_l^m\|_0^2 + \frac{1}{2} (1 + \frac{K\delta t}{\rho_g}) \|\nabla r_l^{m+1}\|_0^2 + \frac{1}{2} \frac{K\delta t}{\rho_g} \|\nabla c_g^m\|_0^2.
\end{aligned} \tag{B.52}$$

The above inequality leads to

$$(1 - \frac{K\delta t}{\rho_g}) \|\nabla r_l^{m+1}\|_0^2 \leq \|\nabla r_l^m\|_0^2 + \frac{K\delta t}{\rho_g} \|\nabla c_g^m\|_0^2. \tag{B.53}$$

Taking the summation from 0 to  $N-1$ , we have

$$\|\nabla r_l^j\|_0^2 \leq \left(1 - \frac{K\delta t}{\rho_g}\right)^{-N} (\|\nabla r_l^0\|_0^2 + \frac{K\delta t}{\rho_g} \sum_{m=0}^{N-1} \|\nabla c_g^m\|_0^2) \tag{B.54}$$

for all  $0 \leq j \leq N$ . Since  $\delta t = T/N$ , we have

$$(1 - \frac{K_g \delta t}{\rho_g})^{-N} = (1 - \frac{K_g T}{N \rho_g})^{-N} \leq \exp(\frac{K_g T}{\rho_g})$$

Employing the above inequality to (B.54), the proof is completed. Q.E.D.

## B.5 Passage to limit $\delta t \rightarrow 0$

Let us define

$$r_{l,\delta} : [0, T] \rightarrow H^1(\Omega), \quad r_{l,\delta}(t) = r_l^j \quad \text{if } t \in ((j-1)\delta t, j\delta t], \tag{B.55}$$

$$r_{l,h} : [0, T] \rightarrow H^1(\Omega), \quad r_{l,h}(t) = \frac{t - (j-1)\delta t}{\delta t} r_l^j + \frac{j\delta t - t}{\delta t} r_l^{j-1} \quad \text{if } t \in ((j-1)\delta t, j\delta t], \tag{B.56}$$

$$c_{dis,\delta} : [0, T] \rightarrow H^1(\Omega), \quad c_{g,\delta}(t) = c_g^j \quad \text{if } t \in ((j-1)\delta t, j\delta t], \tag{B.57}$$

$$c_{s,\delta} : [0, T] \rightarrow H^1(\Omega), \quad c_{s,\delta}(t) = c_s^j \quad \text{if } t \in ((j-1)\delta t, j\delta t] \tag{B.58}$$

$$c_{k,\delta} : [0, T] \rightarrow H^1(\Omega), \quad c_{k,\delta}(t) = c_k^j \quad \text{if } t \in ((j-1)\delta t, j\delta t] \tag{B.59}$$

$$\begin{aligned}
& c_{dis,h} : [0, T] \rightarrow H^1(\Omega), \\
& c_{dis,h}(t) = \frac{t - (j-1)\delta t}{\delta t} c_g^j + \frac{j\delta t - t}{\delta t} c_g^{j-1} \quad \text{if } t \in ((j-1)\delta t, j\delta t],
\end{aligned} \tag{B.60}$$

$$\begin{aligned}
& c_{s,h} : [0, T] \rightarrow H^1(\Omega), \\
& c_{s,h}(t) = \frac{t - (j-1)\delta t}{\delta t} c_s^j + \frac{j\delta t - t}{\delta t} c_s^{j-1} \quad \text{if } t \in ((j-1)\delta t, j\delta t],
\end{aligned} \tag{B.61}$$

$$\begin{aligned}
& c_{k,h} : [0, T] \rightarrow H^1(\Omega), \\
& c_{k,h}(t) = \frac{t - (j-1)\delta t}{\delta t} c_k^j + \frac{j\delta t - t}{\delta t} c_k^{j-1} \quad \text{if } t \in ((j-1)\delta t, j\delta t],
\end{aligned} \tag{B.62}$$

$$c_{dis,\delta-} : [0, T] \rightarrow H^1(\Omega), \quad c_{dis,\delta}(t) = c_g^{j-1} \quad \text{if } t \in ((j-1)\delta t, j\delta t] \tag{B.63}$$

$$c_{s,\delta-} : [0, T] \rightarrow H^1(\Omega), \quad c_{s,\delta-}(t) = c_s^{j-1} \quad \text{if } t \in ((j-1)\delta t, j\delta t] \quad (\text{B.64})$$

$$c_{k,\delta-} : [0, T] \rightarrow H^1(\Omega), \quad c_{k,\delta-}(t) = c_k^{j-1} \quad \text{if } t \in ((j-1)\delta t, j\delta t] \quad (\text{B.65})$$

$$E_{mix,\delta} : [0, T] \rightarrow L^2(S), \quad E_{mix,\delta}(t) = E_{mix}^j \quad \text{if } t \in ((j-1)\delta t, j\delta t] \quad (\text{B.66})$$

$$(r_l c_g)_h : [0, T] \rightarrow H^1(\Omega), \quad (r_l c_g)_h(t) = \frac{t - (j-1)\delta t}{\delta t} r_l^j c_g^j + \frac{j\delta t - t}{\delta t} r_l^{j-1} c_g^{j-1} \quad \text{if } t \in ((j-1)\delta t, j\delta t], \quad (\text{B.67})$$

$$(r_l c_s)_h : [0, T] \rightarrow H^1(\Omega), \quad (r_l c_s)_h(t) = \frac{t - (j-1)\delta t}{\delta t} r_l^j c_s^j + \frac{j\delta t - t}{\delta t} r_l^{j-1} c_s^{j-1} \quad \text{if } t \in ((j-1)\delta t, j\delta t], \quad (\text{B.68})$$

$$(r_l c_k)_h : [0, T] \rightarrow H^1(\Omega), \quad (r_l c_k)_h(t) = \frac{t - (j-1)\delta t}{\delta t} r_l^j c_k^j + \frac{j\delta t - t}{\delta t} r_l^{j-1} c_k^{j-1} \quad \text{if } t \in ((j-1)\delta t, j\delta t], \quad (\text{B.69})$$

With the above notations, the system of discrete equations can be expressed as:

$$\langle \partial_t r_{l,h}, w \rangle + \left( \frac{K_g}{\rho_g} r_{l,\delta} c_{dis,\delta-} \right) = 0 \quad (\text{B.70})$$

$$\begin{aligned} & \langle r_{l,\delta} \partial_t c_{dis,h}, w_g \rangle + D_g(r_{l,\delta} \nabla c_{dis,\delta}, \nabla w_g) + \frac{M_g K_g}{\rho_l} (r_{l,\delta} c_{dis,\delta}, w_g) \\ &= \frac{\beta}{z_s F} (r_{l,\delta} |i_g(E_{mix,\delta})| c_{dis,\delta}, w_g)_{L^2(S)}, \end{aligned} \quad (\text{B.71})$$

$$\langle r_{l,\delta} \partial_t c_{s,h}, w_s \rangle + D_s(r_{l,\delta} \nabla c_{s,\delta}, \nabla w_s) + \frac{1}{z_s F} (r_{l,\delta} |i_s(E_{mix,\delta})| c_{s,\delta}, w_s)_{L^2(S)} = 0, \quad (\text{B.72})$$

$$\langle r_{l,\delta} \partial_t c_{k,h}, w_k \rangle + D_k(r_{l,\delta} \nabla c_{k,\delta}, \nabla w_k) + \frac{1}{z_k F} (r_{l,\delta} |i_k(E_{mix,\delta})| c_{k,\delta}, w_k)_{L^2(S)} = 0 \quad (\text{B.73})$$

Here we collect the boundedness of functions given by (B.58)-(B.66): By Lemmas B.3.2, B.3.3 and B.4.1,  $c_{dis,\delta}, c_{s,\delta}, c_{k,\delta}, c_{dis,\delta-}, c_{s,\delta-}, c_{k,\delta-}$  are uniformly bounded in  $L^2(0, T; H^1(\Omega))$ . Since  $E_{mix,\delta}$  is always bounded in  $B$  for all time,  $E_{mix,\delta}$  is uniformly bounded in  $L^2(0, T; L^2(S))$ . Therefore, there are  $r_l, r_l^*, c_g, c_s, c_k, c_g^*, c_s^*, c_k^*, E_{mix}$  such that there exist subsequences of  $r_{l,\delta}, r_{l,h}, c_{dis,\delta}, c_{s,\delta}, c_{k,\delta}, c_{dis,\delta-}, c_{s,\delta-}, c_{k,\delta-}$  (still denote by same notations) satisfying

$$r_{l,\delta} \rightarrow r_l \quad \text{in } L^2(0, T; H^1(\Omega)) \quad \text{weakly}, \quad (\text{B.74})$$

$$r_{l,h} \rightarrow r_l^* \quad \text{in } L^2(0, T; H^1(\Omega)) \quad \text{weakly}, \quad (\text{B.75})$$

$$c_{dis,\delta} \rightarrow c_g \quad \text{in } L^2(0, T; H^1(\Omega)) \quad \text{weakly}, \quad (\text{B.76})$$

$$c_{s,\delta} \rightarrow c_s \quad \text{in } L^2(0, T; H^1(\Omega)) \quad \text{weakly}, \quad (\text{B.77})$$

$$c_{k,\delta} \rightarrow c_k \quad \text{in } L^2(0, T; H^1(\Omega)) \quad \text{weakly}, \quad (\text{B.78})$$

$$c_{dis,\delta-} \rightarrow c_g^* \quad \text{in } L^2(0, T; H^1(\Omega)) \quad \text{weakly}, \quad (\text{B.79})$$

$$c_{s,\delta-} \rightarrow c_s^* \quad \text{in } L^2(0, T; H^1(\Omega)) \quad \text{weakly}, \quad (\text{B.80})$$

$$c_{k,\delta-} \rightarrow c_k^* \quad \text{in } L^2(0, T; H^1(\Omega)) \quad \text{weakly}, \quad (\text{B.81})$$

$$E_{mix,\delta} \rightarrow E_{mix} \quad \text{in } L^2((0, T) \times S) \quad \text{weakly}. \quad (\text{B.82})$$

For the time derivatives, by Lemma B.4.3, Corollaries B.4.2 and B.4.2, there are  $g_1, g_2, g_3, g_4, g_5, g_6, g_7$  such that

$$\partial_t r_{l,h} \rightarrow g_1 \quad \text{in } L^2(0, T; L^2(\Omega)) \text{ weakly,} \quad (\text{B.83})$$

$$\partial_t c_{dis,h} \rightarrow g_2 \quad \text{in } L^2(0, T; (H^1(\Omega))') \text{ weakly,} \quad (\text{B.84})$$

$$\partial_t c_{s,h} \rightarrow g_3 \quad \text{in } L^2(0, T; (H^1(\Omega))') \text{ weakly,} \quad (\text{B.85})$$

$$\partial_t c_{k,h} \rightarrow g_4 \quad \text{in } L^2(0, T; (H^1(\Omega))') \text{ weakly,} \quad (\text{B.86})$$

$$\partial_t (r_l c_g)_h \rightarrow g_5 \quad \text{in } L^2(0, T; (H^1(\Omega))') \text{ weakly,} \quad (\text{B.87})$$

$$\partial_t (r_l c_s)_h \rightarrow g_6 \quad \text{in } L^2(0, T; (H^1(\Omega))') \text{ weakly,} \quad (\text{B.88})$$

$$\partial_t (r_l c_k)_h \rightarrow g_7 \quad \text{in } L^2(0, T; (H^1(\Omega))') \text{ weakly,} \quad (\text{B.89})$$

**Remark B.5.1** By the  $L^2(0, T; H^1(\Omega))$  boundedness of  $r_{l,\delta} c_{j,\delta}$  for  $j = s, k, dis$ , it is easy to conclude that

$$r_{l,\delta} c_{j,\delta} \rightarrow r_l c_j \quad \text{in } L^2(0, T; H^1(\Omega)) \text{ weakly.} \quad (\text{B.90})$$

**Lemma B.5.1** There are generic constants  $C > 0$  such that

$$\sum_{j=s,k,g} \int_0^T \|r_{l,\delta}(c_{j,\delta} - c_{j,h})\|_0^2 dt \leq C\delta t \quad (\text{B.91})$$

*Proof.* By the definition of (B.55), (B.58), and (B.61), we have

$$\int_{(j-1)\delta t}^{j\delta t} \|r_{l,\delta}(c_{s,\delta} - c_{s,h})\|_0^2 dt = \frac{\delta t}{3} \|r_l^j(c_s^j - c_s^{j-1})\|_0^2 \quad (\text{B.92})$$

Taking the summation from  $j = 1$  to  $j = T/\delta t$ , we get

$$\begin{aligned} \int_0^T \|r_{l,\delta}(c_{s,\delta} - c_{s,h})\|_0^2 dt &= \sum_{j=1}^N \int_{(j-1)\delta t}^{j\delta t} \|r_{l,\delta} c_{s,\delta} - (r_l c_s)_h\|_0^2 dt \\ &= \frac{\delta t}{3} \sum_{j=0}^m \|r_l^j(c_s^j - c_s^{j-1})\|_0^2 \leq C\delta t \end{aligned} \quad (\text{B.93})$$

for some constant  $C > 0$  by Lemma B.4.2. The same proof can be used to show the boundedness for  $r_{l,\delta}(c_{k,\delta} - c_{k,h})$  and  $r_{l,\delta}(c_{dis,\delta} - c_{dis,h})$ . Q.E.D.

**Lemma B.5.2**

$$c_g = c_g^*, \quad c_s = c_s^*, \quad c_k = c_k^*, \quad \text{a.e. in } [0, T] \times \Omega \quad (\text{B.94})$$

*Proof.* Since there is a uniform  $L^\infty$  bound of  $\frac{1}{r_l^m}$  for all  $0 \leq m \leq N$ , there is a constant  $C > 0$  such that

$$C\|c_j^{m+1} - c_j^m\|_0 \leq \|r_l^{m+1}(c_j^{m+1} - c_j^m)\|_0, \quad j = s, k, dis. \quad (\text{B.95})$$

Lemma B.4.2 directly leads to the desired result. Q.E.D.

**Remark B.5.2** By a classical argument, see for instance [113], we have

$$g_1 = \partial_t r_l, \quad g_2 = \partial_t c_g, \quad g_3 = \partial_t c_s, \quad g_4 = \partial_t c_k, \quad g_5 = \partial_t (r_l c_g), \quad g_6 = \partial_t (r_l c_s), \quad g_7 = \partial_t (r_l c_k) \quad (\text{B.96})$$

In order to pass the limit in (B.70)-(B.73), we look into (B.72) firstly and take any  $w = v(x)\lambda(t)$ , where  $v \in W^{1,\infty}(\Omega)$  and  $\lambda \in W_0^{1,\infty}(0, T)$ . Then

$$\begin{aligned} & - \int_0^T ((r_l c_s)_h, v) \lambda'(t) dt - \int_0^T (c_{s,\delta} - \partial_t r_{l,h}, v) \lambda(t) dt + \int_0^T D_s(r_{l,\delta} \nabla c_{s,\delta}, \nabla v) \lambda dt \\ & + \frac{1}{z_s F} \int_0^T (r_{l,\delta} |i_s(E_{mix,\delta})|_{c_{s,\delta}}, v)_{L^2(S)} \lambda dt = 0 \end{aligned} \quad (\text{B.97})$$

For the first term in (B.72), we have

$$- \int_0^T ((r_l c_s)_h, v) \lambda'(t) dt \rightarrow - \int_0^T (r_l c_s, v) \lambda'(t) dt = \int_0^T \langle \partial_t (r_l c_s), v \rangle_{(H^1(\Omega))', H^1(\Omega)} \lambda(t) dt. \quad (\text{B.98})$$

Since  $\partial_t r_{l,\delta}$  converges to  $\partial_t r_l$  weakly in  $L^2((0, T) \times \Omega)$  and  $c_{s,\delta}$  converges to  $c_s$  in  $L^2(0, T) \times \Omega$  by Aubin-Lions lemma, we have

$$\int_0^T (c_{s,\delta} - \partial_t r_{l,h}, v) \lambda(t) dt \rightarrow \int_0^T (c_s \partial_t r_l, v) \lambda(t) dt. \quad (\text{B.99})$$

Since  $r_{l,\delta}$  is strongly convergent in  $L^2((0, T) \times \Omega)$  (by Aubin-Lions lemma) and  $\partial_{x_i} c_{s,\delta}$  is weakly convergent in  $L^2((0, T) \times \Omega)$  for any direction  $x_i$ , we have

$$\int_0^T D_s(r_{l,\delta} \nabla c_{s,\delta}, \nabla v) \lambda dt \rightarrow \int_0^T D_s(r_l \nabla c_s, \nabla v) \lambda dt. \quad (\text{B.100})$$

To deal with the fourth term, Theorem 1 in [39] can be applied. By the Rellich-Kondrachov theorem, we have the compact embedding  $H^1(\Omega) \hookrightarrow H^s(\Omega)$  for all  $0 \leq s < 1$ . On the other hand,  $H^s$  is continuously embedded in  $(H^1(\Omega))'$ . Let  $u$  be an arbitrary function defined on  $[0, T] \times \Omega$ . We define  $\sigma_\tau u(t, x) = u(t - \tau, x)$  in  $[\tau, T] \times \Omega$  for  $0 < \tau < T$ . We claim that  $\delta t^{-1} \|r_{l,\delta} c_{s,\delta} - \sigma_{\delta t}(r_{l,\delta} c_{s,\delta})\|_{L^1(\delta t, T; (H^1(\Omega))')}$  is uniformly bounded.

**Lemma B.5.3** There are generic constants  $C_1, C_2 > 0$  such that

$$\|r_{l,\delta} c_{s,\delta} - \sigma_{\delta t}(r_{l,\delta} c_{s,\delta})\|_{L^1(\tau, T; (H^1(\Omega))')} \leq C_1 \delta t, \quad \|r_{l,\delta} c_{k,\delta} - \sigma_{\delta t}(r_{l,\delta} c_{k,\delta})\|_{L^1(\tau, T; (H^1(\Omega))')} \leq C_2 \delta t \quad (\text{B.101})$$

*Proof.* We prove the bound for  $c_{s,\delta}$  only. By definition of  $c_{s,\delta}$ , we have

$$\begin{aligned} & \|r_{l,\delta} c_{s,\delta} - \sigma_{\delta t}(r_{l,\delta} c_{s,\delta})\|_{L^1(\tau, T; (H^1(\Omega))')} = \int_\tau^T \|r_{l,\delta} c_{s,\delta} - \sigma_{\delta t}(r_{l,\delta} c_{s,\delta})\|_{(H^1(\Omega))'} dt \\ & = \sum_{m=1}^{N-1} \int_{m\delta t}^{(m+1)\delta t} \|r_{l,\delta} c_{s,\delta} - \sigma_{\delta t}(r_{l,\delta} c_{s,\delta})\|_{(H^1(\Omega))'} dt \leq \delta t \sum_{m=0}^{N-1} \|r_s^{m+1} c_s^{m+1} - r_s^m c_s^m\|_{(H^1(\Omega))'} \\ & = \delta t^2 \sum_{m=0}^{N-1} \left\| \frac{r_s^{m+1} c_s^{m+1} - r_s^m c_s^m}{\delta t} \right\|_{(H^1(\Omega))'} \\ & \leq \delta t^2 \sum_{m=0}^{N-1} \left( \left\| \frac{r_s^{m+1} c_s^{m+1} - r_s^m c_s^m}{\delta t} \right\|_{(H^1(\Omega))'}^2 + \frac{1}{2} \right) \leq (C + \frac{1}{2}T) \delta t \end{aligned}$$

for some generic constant  $C > 0$  (by Lemma B.4.3). Q.E.D.

Now using Theorem 1 in [39], we have in particular

$$r_{l,\delta}c_{s,\delta} \rightarrow r_l c_s \quad \text{in } L^2(0, T; H^{\frac{3}{4}}(\Omega)) \quad \text{strongly} \quad (\text{B.102})$$

$$r_{l,\delta}c_{k,\delta} \rightarrow r_l c_k \quad \text{in } L^2(0, T; H^{\frac{3}{4}}(\Omega)) \quad \text{strongly} \quad (\text{B.103})$$

Regarding the trace operator  $T_S : L^2(0, T; H^{\frac{3}{4}}(\Omega)) \rightarrow L^2(0, T; H^{\frac{1}{2}}(S))$  is continuous, we have

$$r_{l,\delta}c_{s,\delta} \rightarrow r_l c_s \quad \text{in } L^2(0, T; H^{\frac{1}{4}}(S)) \quad \text{strongly} \quad (\text{B.104})$$

$$r_{l,\delta}c_{k,\delta} \rightarrow r_l c_k \quad \text{in } L^2(0, T; H^{\frac{1}{4}}(S)) \quad \text{strongly} \quad (\text{B.105})$$

Since  $i_s$  is strongly negative on  $B$ ,  $|i_s| : B \rightarrow L^2(S)$  preserves the continuity and boundedness. Therefore,  $|i_s(E_{mix,\delta})| \rightarrow |i_s(E_{mix})|$  weakly in  $L^2((0, T) \times S)$ . Likewise,  $i_k : B \rightarrow L^2(S)$  is continuous. Therefore,  $i_k(E_{mix,\delta}) \rightarrow i_k(E_{mix})$  weakly in  $L^2((0, T) \times S)$ . The strong convergence of  $r_{l,\delta}c_{s,\delta}$  in  $L^2((0, T) \times S)$  implies that

$$\frac{1}{z_s F} \int_0^T (r_{l,\delta} |i_s(E_{mix,\delta})| c_{s,\delta}, v)_{L^2(S)} \lambda dt \rightarrow \frac{1}{z_s F} \int_0^T (r_l |i_s(E_{mix})| c_s, v)_{L^2(S)} \lambda dt \quad (\text{B.106})$$

Therefore

$$\begin{aligned} & \int_0^T \langle r_l \partial_t c_s, v \rangle_{(H^1(\Omega))', H^1(\Omega)} + \int_0^T D_s(r_l \nabla c_s, \nabla v) \lambda dt \\ & + \frac{1}{z_s F} \int_0^T (r_l |i_s(E_{mix})| c_s, v)_{L^2(S)} \lambda dt = 0 \end{aligned} \quad (\text{B.107})$$

for all  $\lambda \in W_0^{1,\infty}(0, T)$  and for all  $v \in W^{1,\infty}(\Omega)$ . By a totally same argument, we have

$$\begin{aligned} & \int_0^T \langle r_l \partial_t c_k, v \rangle_{(H^1(\Omega))', H^1(\Omega)} \lambda dt + \int_0^T D_k(r_l \nabla c_k, \nabla v) \lambda dt \\ & + \frac{1}{z_k F} \int_0^T (r_l |i_k(E_{mix})| c_k, v)_{L^2(S)} \lambda dt = 0 \end{aligned} \quad (\text{B.108})$$

for all  $\lambda \in W_0^{1,\infty}(0, T)$  and for all  $v \in W^{1,\infty}(\Omega)$ . Moreover, since  $i_s(E_{mix,\delta})c_{s,\delta} + i_k(E_{mix,\delta})c_{k,\delta} = 0$  in  $(0, T) \times S$  for all  $\delta t$  and

$$\int_0^T (i_s(E_{mix,\delta})c_{s,\delta} + i_k(E_{mix,\delta})c_{k,\delta}, v) \lambda dt \rightarrow \int_0^T (i_s(E_{mix})c_s + i_k(E_{mix})c_k, v) \lambda dt \quad (\text{B.109})$$

for all  $\lambda \in W_0^{1,\infty}(0, T)$  and for all  $v \in W^{1,\infty}(\Omega)$ . Therefore the restriction  $i_s(E_{mix})c_s + i_k(E_{mix})c_k = 0$  holds.

Since  $r_{l,\delta}$ ,  $c_{dis,\delta}$  are strongly convergent in  $L^2((0, T) \times \Omega)$ , we have

$$\int_0^T (r_{l,\delta} c_{dis,\delta}, v) \lambda(t) dt \rightarrow \int_0^T (r_l c_g, v) \lambda(t) dt \quad (\text{B.110})$$

Employing the same argument as for  $s$  and  $k$ , we have

$$\begin{aligned} & \int_0^T \langle r_l \partial_t c_g, v \rangle_{(H^1(\Omega))', H^1(\Omega)} + \int_0^T D_g(r_l \nabla c_g, \nabla v) \lambda dt \\ & + \frac{K_g M_g}{\rho_l} \int_0^T (r_{l,\delta} c_{dis,\delta}, v) \lambda(t) dt \rightarrow \int_0^T (r_l c_g, v) \lambda(t) dt - \frac{\beta}{z_s F} \int_0^T (r_l |i_s(E_{mix})| c_s, v)_{L^2(S)} \lambda dt = 0 \end{aligned} \quad (\text{B.111})$$

for all  $\lambda \in W_0^{1,\infty}(0, T)$  and for all  $v \in W^{1,\infty}(\Omega)$ .

To recover the initial conditions, we take  $\lambda \in W^{1,\infty}(0, T)$ ,  $\lambda(T) = 0$ ,  $\lambda(0) \neq 0$ , and  $v \in W^{1,\infty}(\Omega)$ . We consider (B.97) such that all terms are identical except the first one:

$$\int_0^T (\partial_t(r_l c_s)_h, v) \lambda dt = \int_0^T \partial_t((r_l c_s)_h, v) \lambda dt = - \int_0^T ((r_l c_s)_h, v) \lambda'(t) dt - (r_l^0 c_s^0, v) \lambda(0). \quad (\text{B.112})$$

When passing to the limit, we get

$$\begin{aligned} & \int_0^T \langle \partial_t(r_l c_s)_h, v \rangle_{(H^1(\Omega))', H^1(\Omega)} \lambda dt = - \int_0^T (r_l c_s, v) \lambda'(t) dt - (r_l^0 c_s^0, v) \lambda(0) \\ & = \int_0^T \frac{d}{dt} (r_l c_s, v) \lambda dt + (r_l(0) c_s(0), v) \lambda(0) - (r_l^0 c_s^0, v) \lambda(0) \\ & = \int_0^T \langle \partial_t(r_l c_s), v \rangle_{(H^1(\Omega))', H^1(\Omega)} \lambda dt + (r_l(0) c_s(0), v) \lambda(0) - (r_l^0 c_s^0, v) \lambda(0). \end{aligned} \quad (\text{B.113})$$

Therefore

$$(r_l(0) c_s(0), v) = (r_l^0 c_s^0, v), \quad \forall v \in H^1(\Omega) \cap W^{1,\infty}(\Omega)$$

This implies that  $r_l(0) c_s(0) = r_l^0 c_s^0 = r_l^0 c_s^0$ . Since  $r_l^0 > 0$ , by copying the same argument for  $r_l$ ,  $c_k$  and  $c_g$ , we may conclude the above result by the theorem:

**Theorem B.5.1** There exists  $r_l, c_g, c_s, c_k \in L^2(0, T; H^1(\Omega))$ ,  $E_{mix}$  in  $L^2(0, T; B)$  with  $\partial_t r_l, \partial_t c_g, \partial_t c_s, \partial_t c_k \in L^2(0, T; (H^1(\Omega))')$  such that

$$\int_0^T (\partial_t r_l, w) dt + \frac{K_g}{\rho_g} \int_0^T (r_l c_g, w) dt = 0 \quad (\text{B.114})$$

$$\begin{aligned} & \int_0^T \langle r_l \partial_t c_g, w_g \rangle_{(H^1(\Omega))', H^1(\Omega)} dt + \int_0^T D_g(r_l \nabla c_g, \nabla w_g) dt \\ & - \frac{\beta}{z_s F} \int_0^T (r_l |i_s(E_{mix})| c_s, w_s)_{L^2(S)} dt + \frac{K_g M_g}{\rho_l} \int_0^T (r_l c_g, w_g) dt = 0, \end{aligned} \quad (\text{B.115})$$

$$\begin{aligned} & \int_0^T \langle r_l \partial_t c_s, w_s \rangle_{(H^1(\Omega))', H^1(\Omega)} dt + \int_0^T D_s(r_l \nabla c_s, \nabla w_s) dt \\ & + \frac{1}{z_s F} \int_0^T (r_l |i_s(E_{mix})| c_s, w_s)_{L^2(S)} dt = 0, \end{aligned} \quad (\text{B.116})$$

$$\begin{aligned} & \int_0^T \langle r_l \partial_t c_k, w_k \rangle_{(H^1(\Omega))', H^1(\Omega)} dt + \int_0^T D_k(r_l \nabla c_k, \nabla w_s) dt \\ & + \frac{1}{z_k F} \int_0^T (r_l |i_k(E_{mix})| c_k, w_k)_{L^2(S)} dt = 0, \end{aligned} \quad (\text{B.117})$$

satisfying the constraint

$$\int_0^T (i_s(E_{mix})c_s + i_k(E_{mix})c_k, w_e)_{L^2(S)} dt \quad (\text{B.118})$$

for all  $w, w_g, w_s, w_k \in L^2(0, T; H^1(\Omega))$  and for all  $w_e \in L^2((0, T) \times S)$ . Moreover,  $r_l, c_g, c_s, c_k$  satisfy the initial conditions  $r_l(0) = r_l^0, c_g(0) = c_g^0, c_s(0) = c_s^0, c_k(0) = c_k^0$  with  $0 < r_l^0 \leq 1, 0 \leq c_g^0 \leq 1, 0 < c_s^0, c_k^0 \leq 1, r_l^0, c_g^0, c_s^0, c_k^0 \in H^1(\Omega)$ .

**Remark B.5.3** The solution  $(r_l, c_g, c_s, c_k, E_{mix})$  is unique by Theorem B.3.2.

## B.6 Several species case

The results for two species case can be generalized to  $N + 1$  species case,  $N > 2$ . Let  $E_j$  be the constants defined in Section 2 with subscripts  $j = s, k_1, \dots, k_N$ , where  $s$  means the ion to be plated and  $k_1, \dots, k_N$  mean other ions involving in the surface reaction. We assume that  $0 > E_{k_1} > \dots > E_s > \dots > E_{k_N}$ . Again, we assume that the chemical reaction satisfying electron balance on the reaction surface  $S \subset \partial\Omega$  and the convective effect in system (3.26)-(3.28) can be neglected. We assume the same regularity for  $r_l$  and  $c_g$  as in two species case. The system of equations can be expressed as

$$\begin{aligned} \partial_t r_l + \frac{K_g}{\rho_g} c_g &= 0 \quad \text{in } \Omega \times (0, T] \\ r_l \partial_t c_g - \nabla \cdot (r_l D \nabla c_g) + \frac{K_g M_g}{\rho_l} r_l c_g &= 0 \quad \text{in } \Omega \times (0, T] \\ \partial_t (r_l \Theta) - \nabla \cdot (r_l D \nabla \Theta) &= 0 \quad \text{in } \Omega \times (0, T] \end{aligned} \quad (\text{B.119})$$

subject to the boundary conditions

$$-D_j \frac{\partial c_j}{\partial \mathbf{n}} = \frac{|I_j|}{z_j F}, \quad \text{on } S \times (0, T], \quad \frac{\partial c_j}{\partial \mathbf{n}} = 0, \quad \text{on } (\partial\Omega \setminus S) \times (0, T] \quad (\text{B.120})$$

for  $j = s, k_1, \dots, k_N$ , and

$$-D_g \frac{\partial c_g}{\partial \mathbf{n}} = \frac{\beta |I_s|}{z_s F}, \quad \text{on } S \times (0, T], \quad \frac{\partial c_g}{\partial \mathbf{n}} = 0, \quad \text{on } (\partial\Omega \setminus S) \times (0, T] \quad (\text{B.121})$$

The initial conditions are given by  $r_l(0) = r_l^0 \in H^1(\Omega), c_j(0) = c_j^0 \in H^1(\Omega)$  satisfying

$$0 < c_j^0 \leq 1, \quad 0 < r_l^0 \leq 1, \quad \text{in } \Omega \quad (\text{B.122})$$

for  $j = g, s, k_1, \dots, k_N$ . In the above  $\Theta = (c_s, c_{k_1}, \dots, c_{k_N})^T$ . The constraint for electrons balance reads

$$I_s + \sum_{l=1}^N I_{k_l} = 0. \quad (\text{B.123})$$

Here, we omit the semi-discrete scheme for solving  $r_l$  and  $c_g$  since there is nothing different from the two-species case. The time-discrete problem for species  $j = s, k_1, \dots, k_N$  can be expressed as:

$$\frac{r_l^{m+1}(c_j^{m+1} - c_j^m)}{\delta t} - \nabla \cdot (D_j r_l^{m+1} \nabla c_j^{m+1}) = 0 \quad (\text{B.124})$$

with boundary conditions on  $S$

$$-D_j \frac{\partial c_j^{m+1}}{\partial \mathbf{n}} = \frac{1}{z_j F} |i_j(E_{mix}^{m+1})| c_j^{m+1}, \quad (\text{B.125})$$

where

$$\begin{aligned} i_j(E_{mix}^{m+1}) &= L_j \left( \exp \left( \frac{\alpha_j z_j F (E_{mix}^{m+1} - E_j)}{R\theta} \right) - \exp \left( \frac{-\beta_j z_j F (E_{mix}^{m+1} - E_j)}{R\theta} \right) \right), \\ \sum_j i_j(E_{mix}^{m+1}) c_j^{m+1} &= 0 \end{aligned} \quad (\text{B.126})$$

for  $j = s, k_1, k_2, \dots, k_N$ . In the following, we define  $i_j^{m+1} := |i_j(E_{mix}^{m+1})|$ .

Now we define the weak problem for the time-discrete problem:

**Problem**  $(\widetilde{P}_{c_j})$

Find  $c_j^{m+1}$ ,  $j = s, k_1, k_2, \dots, k_N \in H_{r_l^{m+1}}^2(\Omega)$  such that

$$\begin{aligned} &\frac{1}{\delta t} (c_j^{m+1}, w_j)_{r_l^{m+1}} + D_j (\nabla c_j^{m+1}, \nabla w_j)_{r_l^{m+1}} + \frac{1}{z_j F} (r_l^{m+1} i_j^{m+1} c_j^{m+1}, w_j)_{L^2(S)} \\ &= \frac{K}{\rho_l} (c_g^{m+1} c_j^m, w_j)_{r_l^{m+1}} + \frac{1}{\delta t} (c_j^m, w_j)_{r_l^m} \end{aligned} \quad (\text{B.127})$$

subject to the constraint

$$\sum_j \int_S i_j(E_{mix}^{m+1}) c_j^{m+1} w_j d\sigma = 0 \quad (\text{B.128})$$

for all  $w_j \in H^1(\Omega)$ .

Regarding the argument given in the two species case, we need only to show the existence and uniqueness of the fixed point for solving  $E_{mix}^{m+1}$  by iteration algorithm. Firstly, we shall justify the solvability for  $E_{mix}^{m+1}$  for pointwisely given  $c_j^{m+1}$  on  $S$ ,  $j = s, k_1, \dots, k_N$ . Since Theorem 4 in [73] guarantees that there are  $\eta_j^{m+1} > 0$  such that  $c_j^{m+1} \geq \eta_j^{m+1}$  for  $j = s, k_1, \dots, k_N$ , we have

**Lemma B.6.1** There is one and only one root  $E \in [E_{k_N}, E_{k_1}]$  satisfying

$$\sum_j i_j(E) (c_j) = 0 \quad (\text{B.129})$$

for given  $c_j \geq \eta_j^{m+1}$ ,  $j = s, k_1, \dots, k_N$ .

*Proof.* Let  $f(E) = \sum_j i_j(E) (c_j)$ . Obviously, we have

$$f(E_{k_1}) > 0, \quad f(E_{k_N}) < 0 \quad (\text{B.130})$$

The continuity of  $f$  implies that there is a root in  $[E_{k_N}, E_{k_1}]$ . Differentiating  $f$  with respect to  $E$ , we have

$$f'(E) = \sum_{j=1}^N \left( \alpha_{k_j} L_{k_j} e^{\alpha_{k_j}(E-E_{k_j})} + \beta_{k_j} L_{k_j} e^{-\beta_{k_j}(E-E_{k_j})} \right) + \alpha_s L_s e^{\alpha_s(E-E_s)} + \beta_s L_s e^{-\beta_s(E-E_s)} > 0 \quad (\text{B.131})$$



for all  $E \in (E_{k_N}, E_{k_1})$ . This implies that  $f(E)$  is strictly monotone. Therefore, the root is unique. Q.E.D.

Let us define  $\Lambda_1 : B \rightarrow \mathbf{H}_N := W_{\eta_s}^{m+1} \times W_{\eta_{k_1}}^{m+1} \times \cdots \times W_{\eta_{k_N}}^{m+1}$  such that  $\Lambda_1(E)$  is the set of solutions to  $(\widetilde{P}_{c_j})$  when letting  $E_{mix}^{m+1} = E$ .

**Lemma B.6.2**  $\Lambda_1$  is a bounded operator.

*Proof.* The boundedness of  $\Lambda_1$  can be shown by the same argument as in Lemma B.3.3. Q.E.D.

By Corollary 7.3 in [11]:

**Lemma B.6.3** The trace operator  $T_N : \mathbf{H}_N \rightarrow (L^2(S))^{N+1}$  is compact.

Finally, we define  $\Lambda_2 : T_N(\mathbf{H}_N) \rightarrow B$  by

$$\Lambda_2 : (c_s, c_{k_1}, \dots, c_{k_N}) \mapsto E,$$

where  $E$  satisfying  $\sum_j i_j(E) c_j = 0$  for  $j = s, k_1, \dots, k_N$ .

**Lemma B.6.4**  $\Lambda_2$  is a bounded operator.

*Proof.* Let  $\chi = (c_s, c_{k_1}, \dots, c_{k_N}) \in T_N(\mathbf{H}_N)$ , we have  $E_{k_N} \leq \Lambda_2(\chi) \leq E_{k_1}$ . This implies that

$$\|\Lambda_2(\chi)\|_{L^2(S)}^2 \leq \|E_{k_N}\|_{L^2(S)}^2 \leq M \sum_j \|\eta_j^{m+1}\|_0^2 \leq M \sum_j \|c_j\|_0^2 \leq M \sum_j \|c_j\|_1^2 \quad (\text{B.132})$$

for some constant  $M > 0$ . This completes the proof. Q.E.D.

Defining  $\Lambda = \Lambda_2 \circ T_N \circ \Lambda_1$ , we have

**Proposition B.6.1** The operator  $\Lambda : B \rightarrow B$  has a fixed point.

Now the existence result for two species case can be generalized to several species case:

**Theorem B.6.1** There exist unique  $r_l, c_g, c_j \in L^2(0, T; H^1(\Omega))$ ,  $E_{mix} \in L^2(0, T; B)$  with  $\partial_t r_l, \partial_t c_g, \partial_t c_j \in L^2(0, T; (H^1(\Omega))')$  such that

$$\int_0^T (\partial_t r_l, w) dt + \frac{K_g}{\rho_g} \int_0^T (r_l c_g, w) dt = 0 \quad (\text{B.133})$$

$$\begin{aligned} & \int_0^T \langle r_l \partial_t c_g, w_g \rangle_{(H^1(\Omega))', H^1(\Omega)} dt + \int_0^T D_g (r_l \nabla c_g, \nabla w_g) dt \\ & - \frac{\beta}{z_s F} \int_0^T (r_l |i_s(E_{mix})| c_s, w_s)_{L^2(S)} dt + \frac{K_g M_g}{\rho_l} \int_0^T (r_l c_g, w_g) dt = 0, \end{aligned} \quad (\text{B.134})$$

$$\begin{aligned} & \int_0^T \langle \partial_t (r_l c_j), w_j \rangle_{(H^1(\Omega))', H^1(\Omega)} + \int_0^T D_j (r_l \nabla c_j, \nabla w_j) dt \\ & + \frac{1}{z_j F} \int_0^T (r_l |i_j(E_{mix})| c_j, w_j)_{L^2(S)} dt = \frac{K}{\rho_l} \int_0^T (r_l c_g c_j, w_j) dt, \end{aligned} \quad (\text{B.135})$$

satisfying the constraint

$$\sum_j \int_0^T (i_j(E_{mix}) c_s, w_e)_{L^2(S)} dt \quad (\text{B.136})$$

for all  $w, w_g, w_j \in L^2(0, T; H^1(\Omega))$  and for all  $w_e \in L^2((0, T) \times S)$ . Moreover,  $r_l, c_g, c_j$  satisfy the initial conditions  $r_l(0) = r_l^0, c_g(0) = c_g^0, c_j(0) = c_j^0$  with  $0 < r_l^0 \leq 1, 0 \leq c_g^0 \leq 1, 0 < c_j^0 \leq 1, r_l^0, c_g^0, c_j^0 \in H^1(\Omega)$ .



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