

On the perturbation solution of interface-reaction controlled diffusion in solids

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Abstract Insertion of species A into species B forms a product P through two kinetic processes, namely, (1) the chemical reaction between A and B that occurs at the B-P interface, and (2) the diffusion of species A in product P. These two processes are symbiotic in that the chemical reaction provides the driving force for the diffusion, while the diffusion sustains the chemical reaction by providing sufficient reactant to the reactive interface. In this paper, a mathematical framework is developed for the coupled reaction-diffusion processes. The resulting system of boundary and initial value problem is solved analytically for the case of interface-reaction controlled diffusion, i.e., the rate of diffusion is much faster than the rate of chemical reaction at the interface so that the final kinetics are limited by the interface chemical reaction. Asymptotic expressions are given for the velocity of the reactive interface and the concentration of diffusing species under two different boundary conditions.

Keywords Interface · Diffusion · Chemical reaction · Perturbation

1 Introduction

In many processes, diffusion and chemical reactions are coupled. Examples of such processes include, to name a few, dissolution or crystal growth at the interface between minerals and aqueous solution [1], radionuclide release [2], multi-component glass dissolution [3], selective oxidation of Cr-Fe alloys [4], etc. There is also a class of problems in heat transfer that are analogous to such coupled reaction-diffusion phenomena, for example, melting of ice and solidification [5–9].

When chemical reaction and diffusion occur in solid, they often produce volumetric change. Such volumetric change, if not accommodated by appropriate deformation,

mechanical stresses will be generated, which will in turn affect the diffusion and the chemical reaction [10–14]. In a class of such problems [15–24], the diffusion species first reacts chemically with the host solvent to form a third phase (product), and the reaction occurs mainly on the interface between the solvent and this third phase. The reaction is sustained by the diffusion species through the newly formed third phase material. A common feature of these problems is the moving boundary. In addition to solving the diffusion equation for the concentration of the diffusion species, the motion of the interface must also be solved simultaneously with the diffusion equation. Since the chemical reaction takes place at the interface, the kinetics of the interface chemical reaction dictates the interface motion. Kinetic analysis of these phenomena can be greatly simplified by the identification of rate-limiting processes, i.e., the slow steps among those occurring in sequence and fast steps among those occurring in parallel. Clearly, there are three regimes. First, the interface chemical reaction rate is much faster than the rate of diffusion, which means that the velocity of the interface can be assumed infinitely large, thus one only needs to solve the diffusion equation. Second, the interface chemical reaction rate is comparable to the rate of diffusion. In this case, both the interface velocity and the diffusion equation must be solved together. The third regime is when the interface chemical reaction rate is much slower than the rate of diffusion, which means that the diffusion is controlled by the interface chemical reaction. In this paper, we will focus on this third regime.

We will begin by derive the boundary/initial value problem governing the diffusion and the interface motion based on a model binary system. Then, under the assumption that the interface chemical reaction rate is much slower than the diffusion rate, we derive asymptotic solutions to two different types of boundary conditions. Finally, some concluding remarks are given.

2 Problem Statement

Consider a solid film of initial thickness h . For simplic-

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ity, we assume the film extends to infinity in the x_1 - and x_2 -directions as shown in Fig. 1. The film is made of β -phase material composed of species B. Let the top surface of the film be in contact with an α -phase material composed of species A. We assume that under either their chemical affinity, or certain external driving forces, species A chemically reacts with species B at their interface according to the following equation



where x_0 is the stoichiometric coefficients of the reaction. The product $P = A_{x_0}B$ will be called the γ -phase. Since this reaction consumes species B, the film will become thinner, and a β - γ interface is formed. This β - γ interface will keep moving in the negative x_3 -direction if sufficient species A can be supplied to the β - γ interface to sustain the reaction described by Eq. (1). This is possible when either a large enough concentration or large enough flux of species A is prescribed at the α - γ interface, assuming that species A can diffuse through the γ -phase. Our main interest in this paper is to find the velocity of the β - γ interface and the distribution of species A in the γ -phase when either the concentration or the flux of species A is given at the α - γ interface. For simplicity, we will assume that the β -phase is impervious to species A and is fully converted into the γ -phase at the β - γ interface via the interfacial chemical reaction equation (1).

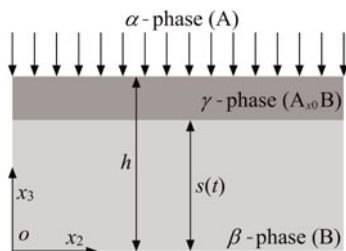


Fig. 1 Reaction at a moving boundary

For convenience, the instantaneous location of the β - γ interface is denoted by $x_3 = s(t)$. Here the Lagrangian (reference) frame is used, and $x_i, i = 1, 2, 3$ are the Lagrangian coordinates. Therefore, $x_3 = h$ describes the location of the α - γ interface at any given time.

Let x_{\max} be the solubility of A in the β -phase (the maximum number of moles of species A that each mole of the β -phase is capable of containing), and x be the deviation of species A from the stoichiometric composition of the γ -phase. We may then introduce the molar fraction as [14],

$$c(x_3, t) = \frac{x + x_0}{x_{\max}}, \text{ for } s(t) < x_3 < h, \tag{2}$$

to describe the deviation from stoichiometry of A in the γ -phase, which is also a measure of the concentration of species A in the nonstoichiometric state of the γ -phase, i.e.,

$A_{x_0+x}B$. Clearly, we have $0 \leq c(x_3, t) \leq 1$. If the reaction described by Eq. (1) is irreversible, i.e., the γ -phase can not be dissolved, we have $x_0/x_{\max} \leq c(x_3, t) \leq 1$. For $0 \leq c(x_3, t) \leq x_0/x_{\max}$, one must have $-x_0 \leq x \leq 0$, which means depletion of A from the γ -phase. For brevity, we will write $c(x_3, t) = c$ in the rest of this paper, unless indicated otherwise.

The molar fraction c can be related to the molar concentration $\rho_A(x_3, t)$ if the molar volume V of the mixture $A_{x_0+x}B$ is known, i.e.,

$$\rho_A(x_3, t) = \frac{x_{\max}c}{V}. \tag{3}$$

In a similar manner, one can show that

$$\begin{aligned} \rho_P(x_3, t) &= \frac{1}{V}, \quad s(t) < x_3 < h, \\ \rho_B(x_3, t) &= \frac{1}{V_m^B}, \quad x_3 < s(t), \end{aligned} \tag{4}$$

where V_m^B is the molar volume of species B in the β -phase. Molar volume of the mixture $A_{x+x_0}B$ is given by

$$V = JV_m^B, \tag{5}$$

where V_m^B is the instantaneous molar volume (or current volume) of the mixture $A_{x+x_0}B$, and J is the Jacobian of the deformation from the initial β -phase to the current state.

The rate of the surface chemical reaction at the interface $x_3 = s(t)$ can be written as

$$R_p = k_f \left(\rho_A - \frac{x_0}{JV_m^B} \right)^m (\rho_B)^n - k_b \rho_P, \quad x_3 = s(t), \tag{6}$$

where m and n are the orders of chemical reaction at the interface that should be determined by experimental measurements. The rate R_p gives the moles of the product $A_{x_0}B$ produced per unit area per unit time, or rate of production of the product $A_{x_0}B$ per unit area in terms of moles. In the above, k_f and k_b are the rate constants for the forward and backward reactions, respectively. We note that in order to ensure the spontaneous forward reaction, the molar concentration of species A, i.e., ρ_A should be greater than a threshold value x_0/JV_m^B , where x_0 is the minimum molar fraction to form γ -phase $A_{x_0}B$. All the molar concentrations ρ_A, ρ_B and ρ_P in Eq. (6) are evaluated at the β - γ interface $x_3 = s(t)$. Since the molar concentrations may not be continuous across the interface, we assume that ρ_B is the molar concentration of B evaluated at the β -phase side of the β - γ interface, while ρ_A and ρ_P are evaluated at the γ -phase side of the β - γ interface, i.e.,

$$\begin{aligned} \rho_B &= \rho_B(s^-(t), t), \\ \rho_A &= \rho_A(s^+(t), t), \\ \rho_P &= \rho_P(s^+(t), t), \end{aligned} \tag{7}$$

Making use of Eqs. (3)–(5) in Eq. (6) leads to

$$R_p = k_f^c \bar{R}_p(c), \tag{8}$$

where

$$\bar{R}_p = \left(\frac{x_{\max}c - x_0}{J} \right)^m - \frac{k_b^e}{k_f^e J} \tag{9}$$

is a dimensionless function, $k_f^e = k_f/(V_m^B)^{m+n}$ and $k_b^e = k_b/V_m^B$ are the effective forward and backward rate constants, respectively. Their dimension is moles per unit area per unit time.

Next, let μ be the chemical potential, or more precisely the diffusion potential of A in the γ -phase. Then, the flux of species A in the x_3 -direction is then given by

$$J_3 = -\frac{Dx_{\max}c}{R_gTV_m^B} \frac{\partial \mu}{\partial x_3}, \tag{10}$$

where D is the diffusivity coefficient A in the γ -phase, R_g is the standard gas constant, and T is the absolute temperature in Kelvin. The continuity equation in the γ -phase is given by

$$\frac{x_{\max}\partial c}{V_m^B\partial t} + \frac{\partial J_3}{\partial x_3} = 0, \quad s(t) < x_3 < h. \tag{11}$$

Substituting Eq. (10) into Eq. (11) leads to

$$\frac{\partial c}{\partial t} - \frac{1}{R_gT} \frac{\partial}{\partial x_3} \left(Dc \frac{\partial \mu}{\partial x_3} \right) = 0, \quad s(t) < x_3 < h. \tag{12}$$

Since all species B are converted into the γ -phase at the β - γ interface, the production of R_p moles of the γ -phase ($A_{x_0}B$) will consume x_0R_p moles of species A which must be supplied by the flux of A into the interface, i.e., the mass balance of species A near the β - γ interface gives

$$J_3 = -x_0R_p, \quad x_3 = s(t), \tag{13}$$

where a negative sign is added because the flux given by Eq. (10) is in the negative x_3 -direction.

At the γ - α interface ($x_3 = h$), the boundary condition can be prescribed either for the concentration or the flux of species A, i.e.,

$$c = c_0 \quad \text{or} \quad J_3 = -\frac{Dx_{\max}c}{R_gTV_m^B} \frac{\partial \mu}{\partial x_3} = J_0, \quad x_3 = h. \tag{14}$$

In addition, initial conditions may be prescribed

$$c(x_3, 0) = 0, \quad s(0) = h. \tag{15}$$

Combination of Eqs. (12)–(15) yields a boundary/initial value for the distribution of $c(x_3, t)$ in the γ -phase. The problem can be solved if the interface location $s(t)$ is known. To obtain the equation for $s(t)$, we note that the production of R_p moles of the γ -phase ($A_{x_0}B$) will consume R_p moles of species B which must be supplied by the motion of the β - γ interface. Therefore, the mass balance of species B dictates the speed of the β - γ interface,

$$v(t) \equiv \dot{s}(t) = -V_m^B R_p, \quad x_3 = s(t), \tag{16}$$

where the negative sign indicates that the interface is moving in the negative x_3 -direction.

The above equations and boundary/initial conditions form a boundary/initial moving problem involving two unknowns $c(x_3, t)$ and $s(t)$. Analytical solution to this nonlinear moving boundary problem system is rather challenging. In what follows, we will attempt an asymptotic solution under certain assumptions.

First, we will adopt a simplified stress-dependent chemical potential by assuming that the deformation is linearly elastic, both the elastic strain and the eigenstrain (strain due to compositional change) are small, and the elastic moduli do not change with non-stoichiometry [14],

$$\mu(\sigma, c) = \mu_0^0 + R_gT \lg(\gamma c) - \eta V_m^B \sigma_{kk}, \tag{17}$$

where μ_0^0 is a constant representing the chemical potential at a standard state, and γ is the activity coefficient which is assumed constant here (dilute concentration). The stress tensor σ_{ij} is the Cauchy stress that is generated by the compositional change in the γ -phase.

Further, we assume small strain and linear elastic deformation. It then follows from the Hooke's law that

$$\sigma_{ij} = \frac{E}{(1+\nu)(1-2\nu)} \left[(1-2\nu)(\varepsilon_{ij} - \eta x_{\max}c \delta_{ij}) + \nu(\varepsilon_{kk} - 3\eta x_{\max}c) \delta_{ij} \right], \tag{18}$$

where E is the Young's modulus, ν is the Poisson's ratio, and ε_{ij} is the total elastic strain, all are of the γ -phase, and η is the coefficient of compositional expansion (CCE) [14]. For the one-dimensional problem considered here, the total strain is non-zero only in the x_3 -direction. Furthermore, the normal stress in the x_3 -direction must vanish. Consequently, one can show that

$$\begin{aligned} \varepsilon_{ij} &= \frac{1+\nu}{1-\nu} \eta x_{\max}c \delta_{i3} \delta_{j3}, \\ \sigma_{33} &= 0, \\ \sigma_{11} = \sigma_{22} &= -\frac{E\eta x_{\max}c}{1-\nu}. \end{aligned} \tag{19}$$

It then follows from Eq. (19) that the chemical potential in Eq. (17) can be reduced to

$$\mu(\sigma, c) = \mu_0^0 + R_gT (\lg(\gamma c) + 2\bar{\eta}c), \tag{20}$$

where

$$\bar{\eta} = \frac{V_m^B E \eta^2 x_{\max}}{R_g T (1-\nu)} \tag{21}$$

is the dimensionless effective CCE.

For small strain deformation, the total Jacobian can be written as $J = 1 + \varepsilon_{kk}$. It then follows from substituting Eq. (19) into Eq. (18) that

$$\varepsilon_{kk} = \nu_0 \eta x_{\max}c \quad \text{with} \quad \nu_0 = \frac{1+\nu}{1-\nu}. \tag{22}$$

Consequently, one has

$$J = 1 + \varepsilon_{kk} = 1 + \nu_0 \eta x_{\max} c. \tag{23}$$

Making use of Eq. (23) in Eq. (9) leads to

$$\bar{R}_p = \left(\frac{x_{\max} c - x_0}{1 + \nu_0 \eta x_{\max} c} \right)^m - \frac{k_b^e}{k_f^e (1 + \nu_0 \eta x_{\max} c)}. \tag{24}$$

Next, we introduce the following dimensionless variables,

$$\bar{t} = \frac{D_0 t}{h^2}, \quad \bar{x} = \frac{x_3}{h}, \quad \bar{s}(\bar{t}) = \frac{s}{h} \left(\frac{h^2 \bar{t}}{D_0} \right), \quad \bar{D} = \frac{D}{D_0}, \tag{25}$$

where D_0 is a constant having the dimension of area/time, and \bar{D} is a dimensionless function representing the concentration dependent part of the diffusion coefficient. In conjunction with Eq. (20), the system of equations Eqs. (12)–(16) can now be casted into dimensionless forms

$$\frac{\partial}{\partial \bar{x}} \left[\bar{D} \left(\frac{\partial c}{\partial \bar{x}} + 2\bar{\eta} c \frac{\partial c}{\partial \bar{x}} \right) \right] = \frac{\partial c}{\partial \bar{t}}, \quad \bar{s}(\bar{t}) < \bar{x} < 1, \tag{26}$$

$$c = c_0 \text{ or } \bar{D} \left(\frac{\partial c}{\partial \bar{x}} + 2\bar{\eta} c \frac{\partial c}{\partial \bar{x}} \right) = \bar{J}_0, \quad \bar{x} = 1, \tag{27}$$

$$\bar{D} (1 + 2\bar{\eta} c) \frac{\partial c}{\partial \bar{x}} = \frac{x_0}{x_{\max}} \beta \bar{R}_p(c), \quad \bar{x} = \bar{s}(\bar{t}), \tag{28}$$

$$\bar{v}(\bar{t}) \equiv \frac{d\bar{s}(\bar{t})}{d\bar{t}} = -\beta \bar{R}_p(c), \quad \bar{x} = \bar{s}(\bar{t}), \tag{29}$$

where $\bar{J}_0 = J_0 V_m^B h / D_0 x_{\max}$ is the prescribed dimensionless flux of species A at the $\gamma - \alpha$ interface $\bar{x} = 1$, and $\beta = k_f^e V_m^B h / D_0$ is a dimensionless parameter that is equivalent to the well-known Biot number in heat transfer. It gives a measure of the relative rates between the chemical reaction at the $\beta - \gamma$ interface and the diffusion of species A in the γ -phase.

For $\bar{D} = 1, \beta \ll 1$, and $c|_{\bar{x}=1} = c_0$, it follows from the Appendix that the asymptotic solutions for small β are given by

$$\bar{v}(\bar{t}) = \frac{d\bar{s}}{d\bar{t}} = -\beta R_0 \exp \left(-\frac{x_0 \beta^2 R_0 R_0' \bar{t}}{x_{\max} (1 + 2\bar{\eta} c_0)} \right), \tag{30}$$

$$c = c_0 - \frac{x_0 \beta R_0 (1 - \bar{x})}{x_{\max} (1 + 2\bar{\eta} c_0)}. \tag{31}$$

Assuming that the backward reaction is negligible, i.e., $k_b = 0$, we have

$$R_0 = \bar{R}_p|_{c=c_0} = \left(\frac{x_{\max} c_0 - x_0}{1 + \nu_0 \eta x_{\max} c_0} \right)^m, \tag{32}$$

$$R_0' = \left. \frac{\partial \bar{R}_p}{\partial c} \right|_{c=c_0} = \frac{(1 + \nu_0 \eta x_0) m x_{\max} R_0}{(1 + \nu_0 \eta x_{\max} c_0) (x_{\max} c_0 - x_0)}.$$

The corresponding non-zero stresses can then be evaluated from Eq. (19) by making use of Eq. (31)

$$\sigma_{11} = \sigma_{22} = -\frac{E \eta x_{\max}}{1 - \nu} \left(c_0 - \frac{x_0 \beta R_0 (1 - \bar{x})}{x_{\max} (1 + 2\bar{\eta} c_0)} \right). \tag{33}$$

Clearly, it is seen from Eq. (30) that, to sustain the downward motion of the $\beta - \gamma$ interface, i.e., $\bar{v}(\bar{t}) < 0$, one must have $R_0 > 0$, which requires $c_0 > x_0 / x_{\max}$, namely, the prescribed concentration at the $\alpha - \gamma$ interface must be greater than the minimum concentration of species A required to form the γ -phase. In addition, we note that although the velocity of the $\beta - \gamma$ interface depends on time, the parameters are typically such that its time-dependence is very weak for small β . The maximum speed of the $\beta - \gamma$ interface achievable under prescribed concentration at the $\alpha - \gamma$ interface is given by

$$\bar{v}_{\max} = \beta R_0|_{c=1} = \beta \left(\frac{x_{\max} - x_0}{1 + \nu_0 \eta x_{\max}} \right)^m. \tag{34}$$

It is seen that the coupling between the diffusion and stress, i.e., non-zero η , slows down the $\beta - \gamma$ interface velocity.

Equation (31) indicates that the concentration of species A in the γ -phase is also independent of time, albeit the size of the γ -phase zone increases with time, i.e., $s(t)$ is not a constant. The maximum concentration is at the $\alpha - \gamma$ interface, and decreases linearly towards the $\beta - \gamma$ interface. The compressive stresses have identical spatial distribution as the concentration of species A. The maximum stress $-E \eta x_{\max} c_0 / (1 - \nu)$ occurs at the $\alpha - \gamma$ interface.

Next, consider the case where the flux is prescribed at $\bar{x} = 1$. Specifically, we assume that

$$\bar{D} \left(\frac{\partial c}{\partial \bar{x}} + 2\bar{\eta} c \frac{\partial c}{\partial \bar{x}} \right) = \bar{J}_0 (1 - c) \text{ at } \bar{x} = 1. \tag{35}$$

This is a linearized Butler–Volmer condition used commonly for electrochemical reaction at the electrode-electrolyte interface. In this case, \bar{J}_0 is effectively the charging rate. Again, we assume $\bar{D} = 1, \beta \ll 1$. It then follows from the Appendix that the asymptotic solutions for small β are given by

$$\begin{aligned} \bar{v}(\bar{t}) &= \frac{d\bar{s}}{d\bar{t}} \\ &= -\beta R_0 \left(1 - \frac{x_0 \beta R_0'}{x_{\max} \bar{J}_0} \right) \exp \left(-\frac{x_0 \beta^2 R_0 R_0' \bar{t}}{x_{\max} (1 + 2\bar{\eta})} \right), \end{aligned} \tag{36}$$

$$c = 1 - \frac{x_0 \beta R_0}{x_{\max}} \left(\frac{1}{\bar{J}_0} + \frac{1 - \bar{x}}{1 + 2\bar{\eta}} \right), \tag{37}$$

where

$$\begin{aligned} R_0 &= \bar{R}_p|_{c=c_0} = \left(\frac{x_{\max} - x_0}{1 + \nu_0 \eta x_{\max}} \right)^m, \\ R_0' &= \left. \frac{\partial \bar{R}_p}{\partial c} \right|_{c=c_0} = \frac{(1 + \nu_0 \eta x_0) m x_{\max} R_0}{(1 + \nu_0 \eta x_{\max}) (x_{\max} - x_0)}. \end{aligned} \tag{38}$$

The corresponding non-zero stresses can then be evaluated from Eq. (19) by making use of Eq. (37),

$$\sigma_{11} = \sigma_{22} = -\frac{E \eta x_{\max}}{1 - \nu} \left[1 - \frac{x_0 \beta R_0}{x_{\max}} \left(\frac{1}{\bar{J}_0} + \frac{1 - \bar{x}}{1 + 2\bar{\eta}} \right) \right]. \tag{39}$$

We note that both R_0 and R'_0 are positive. Therefore, to sustain the downward motion of the β - γ interface, i.e., $\bar{v}(\bar{t}) < 0$, the charging rate must be large enough so that $\bar{J}_0 > x_0\beta R'/x_{\max}$, i.e.,

$$\bar{J}_0 > \frac{x_0\beta R_0 m (1 + \nu_0\eta x_0)}{(x_{\max} - x_0)(1 + \nu_0\eta x_{\max})} \tag{40}$$

According to Eq. (37), the charging rate must also satisfy the inequality below in order to ensure that $c(1, t) > x_0/x_{\max}$, i.e.,

$$\bar{J}_0 > \frac{x_0\beta R_0}{x_{\max} - x_0} \tag{41}$$

Comparison between Eqs. (41) and (40) shows that if (which is typically the case)

$$\frac{m(1 + \nu_0\eta x_0)}{1 + \nu_0\eta x_{\max}} < 1, \tag{42}$$

then the minimum charging rate required is given by Eq. (41). Otherwise, the minimum charging rate required would be given by Eq. (40). Suppose that the materials are such that Eq. (42) holds. Then, the minimum stress induced by using the minimum charging rate can be obtained by substituting

$$\sigma_{\min} = -\frac{E\eta x_0}{1 - \nu} \tag{43}$$

It can be seen from Eqs. (36)–(37) that both the β - γ interface motion and the concentration of species A in γ -phase increase with increasing effective charging rate \bar{J}_0 . The upper limit of β - γ interface motion is, however, independent of charging rate, and is given by

$$\bar{v}_{\max} = \beta R_0 |_{\bar{J}_0 \rightarrow \infty} = \beta \left(\frac{x_{\max} - x_0}{1 + \nu_0\eta x_{\max}} \right)^m \tag{44}$$

To put the above solutions in perspective, numerical results are calculated using the material parameters shown in Table 1. These parameters are fairly good approximations, if one assumes that species A is lithium and species B is crystalline silicon. In the numerical calculations, the Biot number β is taken between 0.01 and 0.2 for our perturbation solutions.

Shown in Fig. 2a is the spatial distribution of concentration of species A in the γ -phase for different values of the prescribed concentration c_0 at the α - γ interface. It is seen that the concentration of species A in the γ -phase is rather uniform, and equals to c_0 . This is expected for small β , for it means that the reaction kinetics at the β - γ interface is so slow that species A reaches its saturation in the γ -phase rather quickly. This is no longer the case when β is large. Figure 2a also shows that the β - γ interface moves faster under higher concentration of species A, an indication that the chemical kinetics at the interface depend on the concentration of the reactants.

Table 1 Material properties used in the numerical model

Elastic constant E/GPa	90.13
Poisson's ratio ν	0.28
Gas constant $R_g/(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$	8.314
Temperature T/K	300
Molar volume of species B $V_m^B/(\text{m}^3 \cdot \text{mol}^{-1})$	1.2052×10^{-5}
Maximum concentration x_{\max}	4.4
Coefficient of compositional expansion (CCE) η	0.2356
Order the chemical reaction m	1
Stoichiometric coefficients of the reaction x_0	0.2

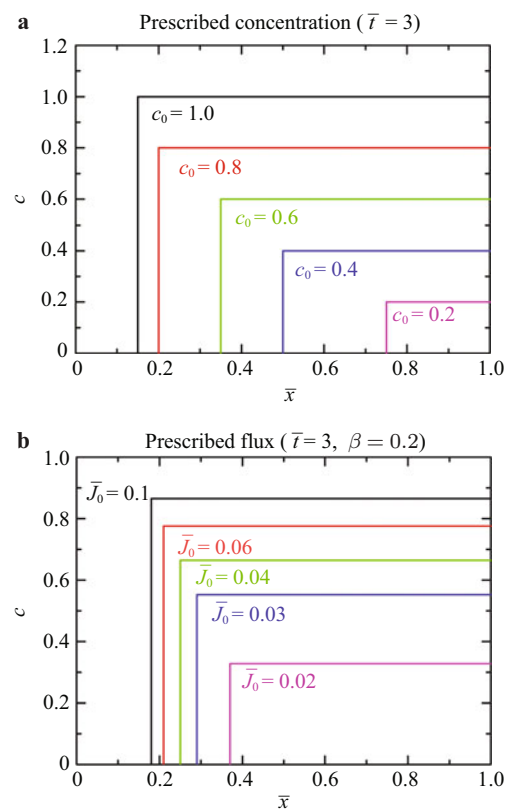


Fig. 2 Concentration of species A in the γ -phase for different values of prescribed **a** c_0 and **b** \bar{J}_0 . The sharp drops in the concentration indicate the locations of the β - γ interface

Similarly, Fig. 2b shows the spatial distribution of concentration of species A in the γ -phase. Similar trends are observed. For example, the concentration of species A in the γ -phase is rather uniform, and the β - γ interface moves faster under higher \bar{J}_0 . One of the differences between prescribing the concentration and prescribing the flux at the α - γ interface is that the concentration does not linearly scale up with \bar{J}_0 . Shown in Fig. 3 is the concentration of species A at the α - γ interface as a function of \bar{J}_0 for different values of β . The results show that under a given value of \bar{J}_0 , a larger β leads to

a smaller c in the γ -phase, which again is expected, because large β means faster chemical kinetics at the β - γ interface. Consequently, species A is consumed faster at the β - γ interface leading to faster interface motion, which lowers the concentration of species A under the same input flux.

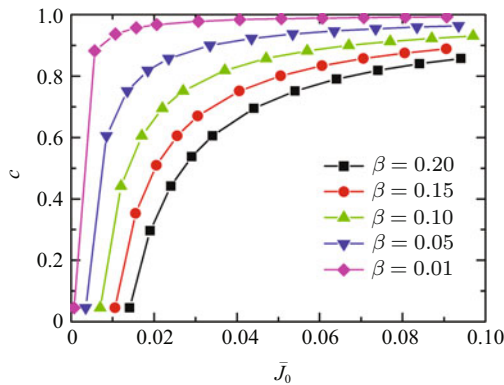


Fig. 3 Concentration of species A at the α - γ interface under prescribed \bar{J}_0

For the values shown in Table 1, it can be shown from Eqs. (30) and (36) that the velocity of the β - γ interface is approximately time-independent in both cases. Shown in Figs. 4a and 4b are the calculated interface speed versus c_0 and \bar{J}_0 , respectively, for different values of β . As expected, the β - γ interface speed is higher for higher values

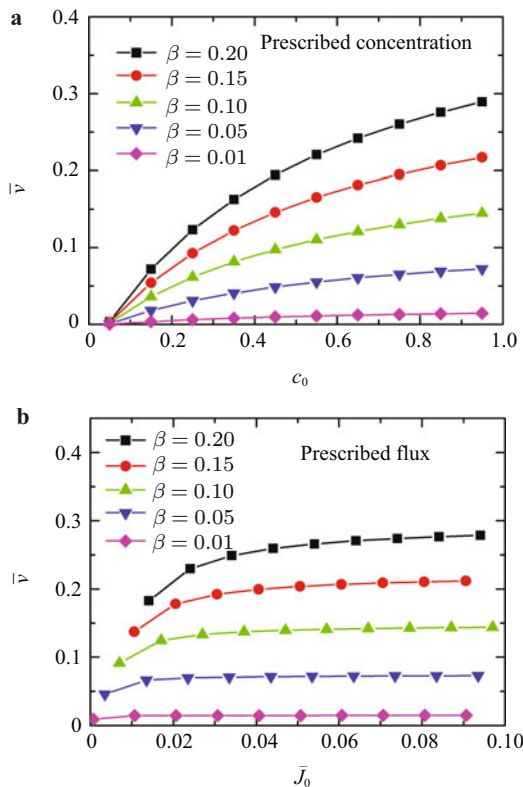


Fig. 4 Speed of the β - γ interface as a function of **a** c_0 and **b** \bar{J}_0

of β , since higher values of β means higher rate of chemical reaction at the interface. If we take $h = 450 \mu\text{m}$ and $D_0 = 10^{-13} \text{m}^2/\text{s}$ [25], then the physical velocity calculated from the results in Fig. 4b is about (0.002–0.06)nm/s depending on the values of β and \bar{J}_0 used. A recent paper reports that the experimentally measured value is $\sim 0.01 \text{nm/s}$ for the insertion of lithium into a Si crystalline film of approximately $450 \mu\text{m}$ thick [26].

We note that the elastic strain increases with increasing c_0 or \bar{J}_0 . For the parameters given in Table 1, the elastic strain can be as high as $\sim 5\%$ when $c_0 \sim 0.1$. This means that higher values of c_0 will generate deformation that is beyond the small strain linear elastic range. Therefore, the small strain assumption used in deriving the above perturbation solution is no longer valid. To account for such large strain, finite deformation theory will be needed [14]. Furthermore, large strain will generate high stresses, which will likely to produce plastic deformation in the γ -phase. So, plasticity will need to be considered as well [14].

3 Summary

A mathematical framework is developed for the coupled reaction-diffusion processes. The resulting system of boundary and initial value problem is solved analytically for the case of interface-reaction controlled diffusion, i.e., the rate of diffusion is much faster than the rate of chemical reaction at the interface so that the final kinetics are limited by the interface chemical reaction. Asymptotic expressions are given for the velocity of the reactive interface and the concentration of diffusing species under two different boundary conditions.

The asymptotic solutions are applied to the insertion of lithium into crystalline silicon film. The results show that a sharp interface is present between the lithiated and unlithiated region. The velocity of this phase interface is almost a constant. In the lithiated region, the concentration of lithium is almost uniform. These results are in good agreement with experimental observations [26].

Finally, we note that although the formulation presented in this paper is general, the asymptotic solutions are valid only for small β , namely, the rate of diffusion of species A in the γ -phase is much faster than the rate of chemical reaction at the interface, so that the kinetics of the system are controlled by the reaction. For intermediate values of β , the nonlinear system of equations can be solved numerically.

Appendix

Consider dimensionless functions $u(x, t)$ and $s(t)$ that satisfy the following system of equations,

$$\frac{\partial}{\partial x} \left(\frac{\partial u}{\partial x} + 2\eta u \frac{\partial u}{\partial x} \right) = \frac{\partial u}{\partial t}, \quad s(t) < x < 1, \tag{A1}$$

$$u = c_0 \quad \text{or} \quad (1 + 2\eta u) \frac{\partial u}{\partial x} = J_0, \quad x = 1, \tag{A2}$$

$$(1 + 2\eta u) \frac{\partial u}{\partial x} = \frac{x_0}{x_{\max}} \beta R(u), \quad x = s(t), \tag{A3}$$

$$v(t) \equiv \frac{ds(t)}{dt} = -\beta R(u), \quad x = s(t). \tag{A4}$$

Without loss of generality, we have assumed that t and x are dimensionless temporal and spatial variable, $R(u)$ is a function of u representing the order of chemical reaction at the interface, and β is the Biot number representing the ratio of the diffusion rate and the reaction rate. The forcing terms are given by either the prescribed dimensionless concentration c_0 or the prescribed dimensionless flux at $x = 1$. In what follows, we seek an asymptotic solution for $\beta \ll 1$.

It is plausible that $s(t)$ is a monotonic function of t . Thus, its inverse function $t(s)$ exists. Therefore, one can then write

$$u(x, t) = u(x, t(s)) = U(x, s). \tag{A5}$$

In other words, the concentration can be treated as a function of two independent variables, x and s , as long as proper chain rules are used for derivatives with respect to t . For example,

$$\frac{\partial u}{\partial t} = \frac{\partial U}{\partial s} \frac{\partial s}{\partial t} = \frac{\partial U}{\partial s} \frac{ds}{dt}, \quad \frac{\partial u}{\partial x} = \frac{\partial U}{\partial x}. \tag{A6}$$

Therefore, Eqs. (A1)–(A4) can be rewritten as

$$\frac{\partial}{\partial x} \left(\frac{\partial U}{\partial x} + 2\eta U \frac{\partial U}{\partial x} \right) = \frac{\partial U}{\partial s} \frac{ds}{dt}, \quad s < x < 1, \tag{A7}$$

$$U = c_0 \text{ or } (1 + 2\eta U) \frac{\partial U}{\partial x} = J_0, \quad x = 1, \tag{A8}$$

$$(1 + 2\eta U) \frac{\partial U}{\partial x} = \frac{x_0}{x_{\max}} \beta R(U), \quad x = s, \tag{A9}$$

$$v(t) \equiv \frac{ds(t)}{dt} = -\beta R(U), \quad x = s. \tag{A10}$$

Substitute Eq. (A10) into Eq. (A7) yields to

$$\frac{\partial}{\partial x} \left(\frac{\partial U}{\partial x} + 2\eta U \frac{\partial U}{\partial x} \right) = -\beta R(U) \frac{\partial U}{\partial s}, \quad s < x < 1, \tag{A11}$$

Combining Eqs. (A8), (A9) and (A11) leads to

$$\frac{\partial}{\partial x} \left(\frac{\partial U}{\partial x} + 2\eta U \frac{\partial U}{\partial x} \right) = -\beta R(U) \frac{\partial U}{\partial s}, \quad s < x < 1, \tag{A12}$$

$$(1 + 2\eta U) \frac{\partial U}{\partial x} = \frac{x_0}{x_{\max}} \beta R(U), \quad x = s, \tag{A13}$$

$$U = c_0 \text{ or } (1 + 2\eta U) \frac{\partial U}{\partial x} = J_0, \quad x = 1. \tag{A14}$$

This is a boundary value problem for the unknown $U(x, s)$. We note that s here is only a parameter. In other words, the system described by Eqs. (A12)–(A14) is an ordinary differential align with boundary conditions prescribed at $x = s$ and $x = 1$. However, because of its nonlinearity, analytical solution to this boundary value problem remains elusive to

the authors. Here, we will attempt an asymptotic solution for $\beta \ll 1$.

To this end, we assume that

$$U = U_0 + \beta U_1, \quad R(U) = R_0 + \beta R'_0 U_1, \tag{A15}$$

where $U_n, n = 0, 1$ are functions of x and s , but do not depend on β explicitly, and

$$R_0 = R(U_0), \quad R'_0 = \left. \frac{dR(U)}{dU} \right|_{U=U_0}. \tag{A16}$$

AI Prescribed concentration

We first consider the problem where the concentration is prescribed at $x = 1$. Substituting Eq. (A15) into Eqs. (A12)–(A14) leads to the following three boundary value problems for U_0 ,

$$\frac{\partial}{\partial x} \left[(1 + 2\eta U_0) \frac{\partial U_0}{\partial x} \right] = 0, \quad s < x < 1, \tag{A17}$$

$$(1 + 2\eta U_0) \frac{\partial U_0}{\partial x} = 0, \quad x = s, \tag{A18}$$

$$U_0 = c_0, \quad x = 1, \tag{A19}$$

for U_1

$$\frac{\partial^2}{\partial x^2} (U_1 + 2\eta U_1 U_0) = -R_0 \frac{\partial U_0}{\partial s}, \quad s < x < 1, \tag{A20}$$

$$\frac{\partial}{\partial x} (U_1 + 2\eta U_0 U_1) = \frac{x_0}{x_{\max}} R_0, \quad x = s, \tag{A21}$$

$$U_1 = 0, \quad x = 1. \tag{A22}$$

Solutions to the above are

$$U_0 = c_0, \quad U_1 = -\frac{x_0 R_0 (1 - x)}{x_{\max} (1 + 2\eta c_0)}, \tag{A23}$$

Substitute Eq. (A23) into Eq. (A10) and keep only terms up to β^2 yields

$$\frac{ds}{dt} = -\beta R_0 \left[1 + \frac{x_0 \beta R'_0 (s - 1)}{x_{\max} (1 + 2\eta c_0)} \right]. \tag{A24}$$

This is an ordinary differential align for $s(t)$. One may assume that $s(0) = 1$. Equation (A24) can then be solve to yield

$$s(t) = 1 + \frac{x_{\max} (1 + 2\eta c_0)}{x_0 \beta R'_0} \times \left[\exp \left(-\frac{x_0 \beta^2 R_0 R'_0 t}{x_{\max} (1 + 2\eta c_0)} \right) - 1 \right]. \tag{A25}$$

The velocity of the interface is then obtained by differentiating Eq. (A25) with respect to time

$$v(t) = \dot{s}(t) = -\beta R_0 \exp \left(-\frac{x_0 \beta^2 R_0 R'_0 t}{x_{\max} (1 + 2\eta c_0)} \right). \tag{A26}$$

To obtain the concentration profile, we substitute Eq. (A23) into Eq. (A15)

$$u = c_0 - \frac{x_0\beta R_0(1-x)}{x_{\max}(1+2\eta c_0)} \tag{A27}$$

AII Prescribed flux

Next, consider the boundary value problem with prescribed flux at $x = 1$, i.e.,

$$(1 + 2\eta u) \frac{\partial u}{\partial x} = J_0 = B(1 - u), \tag{A28}$$

where B is a constant. The expansion given in Eq. (A15) will be used again. This time, the aligns for U_0 are given by

$$\frac{\partial}{\partial x} \left[(1 + 2\eta U_0) \frac{\partial U_0}{\partial x} \right] = 0, \quad s < x < 1, \tag{A29}$$

$$(1 + 2\eta U_0) \frac{\partial U_0}{\partial x} = 0, \quad x = s, \tag{A30}$$

$$(1 + 2\eta U_0) \frac{\partial U_0}{\partial x} + BU_0 = B, \quad x = 1, \tag{A31}$$

for U_1

$$\frac{\partial^2}{\partial x^2} (U_1 + 2\eta U_1 U_0) = -R_0 \frac{\partial U_0}{\partial s}, \quad s < x < 1, \tag{A32}$$

$$\frac{\partial}{\partial x} (U_1 + 2\eta U_0 U_1) = \frac{x_0}{x_{\max}} R_0, \quad x = s, \tag{A33}$$

$$\frac{\partial}{\partial x} (U_1 + 2\eta U_0 U_1) + BU_1 = 0, \quad x = 1. \tag{A34}$$

Solutions to the above are

$$U_0 = 1, \quad U_1 = \frac{x_0}{x_{\max}} \left(\frac{x-1}{1+2\eta} - \frac{1}{B} \right) R_0, \tag{A35}$$

Substitute Eq. (A35) into Eq. (A10), and keep only terms up to β^2 yields

$$\frac{ds}{dt} = -\beta R_0 \left[1 + \frac{x_0\beta R'_0}{x_{\max}} \left(\frac{s-1}{1+2\eta} - \frac{1}{B} \right) \right]. \tag{A36}$$

This is an ordinary differential align for $s(t)$. One may assume that $s(0) = 1$. Equation (A36) can then be solve to yield

$$s(t) = 1 + \frac{(1+2\eta)(x_{\max}/x_0 - \beta R'_0/B)}{\beta R'_0} \times \left[\exp \left(-\frac{x_0\beta^2 R_0 R'_0 t}{x_{\max}(1+2\eta)} \right) - 1 \right]. \tag{A37}$$

The velocity of the interface is then obtained by differentiating equation (A37) with respect to time

$$v(t) = -\beta R_0 \left(1 - \frac{x_0\beta R'_0}{x_{\max}B} \right) \exp \left(-\frac{x_0\beta^2 R_0 R'_0 t}{x_{\max}(1+2\eta)} \right). \tag{A38}$$

To obtain the concentration profile, we substitute Eq. (A35) into Eq. (A15)

$$u = 1 - \frac{x_0\beta R_0}{x_{\max}} \left(\frac{1}{B} + \frac{1-x}{1+2\eta} \right). \tag{A39}$$

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