Shrinking core model for the reaction-diffusion problem in thermo-chemical heat storage

C/T/E Energy Storage - 09

Shrinking Core Model for the Reaction-Diffusion Problem in Thermo-Chemical Heat Storage

Shuiquan Lan[1], Herbert A. Zondag[1, 2], Camilo C.M. Rindt[1,*]

[1] Eindhoven University of Technology, Department of Mechanical Engineering, P.O.Box 513, 5600 MB Eindhoven, The Netherlands.
[2] ECN, Energy Research Centre of the Netherlands, P.O. Box 1, 1755 ZG Petten, The Netherlands.

Corresponding email: C.C.M.Rindt@tue.nl

Keywords: Thermochemical heat storage, Shrinking core model, Reaction diffusion interaction, Lithium sulphate monohydrate, Thermal dehydration

SUMMARY

In this work, we develop a kinetic model to study the dehydration reaction of $Li_2SO_4.H_2O$ single particles involving interaction between the intrinsic chemical reaction and the bulk diffusion. The mathematical framework of the model is based on the shrinking core model. A variable-grid, finite-difference method with fully implicit formulation is used for solving the model. It is found that the Damköhler number $Da = (k_r r_0)/(D_e c_0)$ plays an important role in determining the nature of the diffusion/reaction dynamics. A very small Da value means that the overall reaction is controlled by the intrinsic chemical reaction at the interface, while a very large Da value means that the overall reaction is controlled by the diffusion of water through the product phase. Moreover, the numerical results of fractional conversion calculated in the model are in good agreement with the theoretical analysis under extreme cases in which either diffusion (large Da) or reaction (small Da) dominates the dehydration process. With consideration of numerical solutions at various Da values, it is concluded that both intrinsic reaction and mass diffusion are important in determining the reaction kinetics within a range of Da values between 0.1 and 10.

INTRODUCTION

Dehydration reactions of salt hydrates are of prime importance in various industrial and environmental applications such as thermochemical heat storage. An adequate understanding of the mechanism and kinetics of the reactions is essential to analyse and then to optimize the reaction rate. In this work, the thermal dehydration of lithium sulphate monohydrate (see Eq. 1) is investigated.

$$Li_2SO_4.H_2O(\text{s}) \leftrightarrow Li_2SO_4(\text{s}) + H_2O(g) \tag{1}$$
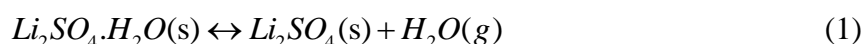
This reaction used to be recommended by the Kinetics Committee of the International Confederation of Thermal Analysis (ICTA) as a material for the study of the reaction kinetics of solid-state reaction. Therefore, its reaction kinetics has been extensively studied using various kinetic models, but significant differences in the Arrhenius parameters have been reported (Brown et al. 1992; Brown et al. 1993; Ferchaud et al. 2012; Kanungo and Mishra

2006). One of the main reasons is the use of different methods of data analysis. It is well known that the complicated process of dehydration is composed of several stages, e.g., the intrinsic reaction of bond breaking, formation of nuclei and their growth, diffusion of gaseous products, and heat transfer. The fact is that, in general, the reaction kinetics is not to be determined by a single mechanism but by a combination of several mechanisms. Unfortunately, kinetic models for the dehydration rate are often simplified to a certain mechanism due to the ease of application. Kinetic studies based on them do not necessarily provide reliable kinetic data.
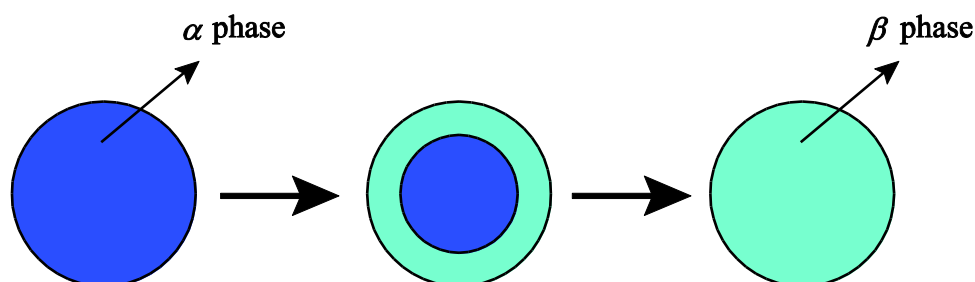

Figure 1: Illustration of the shrinking core model that has been used to describe the dehydration of a salt hydrate particle. A shell of one phase surrounds a core of the other phase, with the interface between the two phases moving inwards.

We want to consider the kinetics of the dehydration reaction in a more fundamental mechanistic level, where the overall reaction is dependent on intrinsic reaction and mass diffusion. The idea of the shrinking core (sharp interface) model is used to describe the thermal dehydration of $Li_2SO_4.H_2O$ salt hydrates. As shown schematically in Fig. 1, the dehydration process of a salt hydrate crystal includes a phase change only at the sharp interface of the core. The particle size does not change but the radius of the core decreases as the reaction proceeds. In the fully hydrated state, the salt hydrate crystal is in the α phase. The dehydration process begins when water vapor at the surface of the particle starts to escape from the crystal structure. The transformation of the salt hydrate (α phase) at the surface promotes the formation of the dehydrated phase (β phase). Next, the adsorbed water that is lost at the surface of the particle is replenished by diffusion of water molecules from the salt hydrate α phase to the surface through the β phase. The dehydration process is complete when all the water from the salt crystal has been lost and the particle consists only of the β phase.

The shrinking core model was first developed by Yagi and Kunii (Yagi and Kunii 1955; Yagi and Kunii 1961) to describe the reactions between gaseous species and solid particles, and has been developed to incorporate various physicochemical phenomena under a variety of conditions (Knorr et al. 2012). A summary of previous work on this model can be found in the article of Gupta and Saha (Gupta and Saha 2003). There are a few applications of this model to a solid-state reaction where the interaction between the interface reaction and mass diffusion is involved simultaneously. One example is about the thermal decomposition of $SrCO_3$ compacts, but the calculation is limited to the pseudo-steady state (Arvanitidis et al. 1999). In other fields of application such as the electrochemistry of the discharging of a metal hydride electrode (Deshpande et al. 2011; Subramanian et al. 2000), metallurgy of the phase transformation (Schuh 2000) and hydrogen storage (Saetre 2006), only the diffusion of gaseous products is considered without reaction at the moving interface. Recently, Cui et al. (Cui et al. 2013) presented a particularly complete model to describe the interface-reaction controlled diffusion in binary solids, such as Li_xSi, which can account for the finite deformation kinetics, diffusion-stress interaction and the interplay between bulk diffusion and intrinsic chemical reaction.

In this paper a shrinking core model involving the intrinsic chemical reaction and bulk diffusion is developed. A variable-grid, finite-difference method with fully implicit formulation is used for solving the governing equations of the model. Numerical solutions under various situations regarding the competion between intrinsic reaction and mass diffusion are presented for discussion.

NUMERICAL MODEL

The dehydration of a spherical salt hydrate particle is assumed to follow the sequence described in Fig. 1. The mass flux of the reversible reaction considered is written as:

$$J_{H_2O} = k_r (1 - \frac{c_c}{c_{eq}}) \tag{2}$$

where k_r is the reaction rate constant at the interface, c_c is the water concentration at the interface and c_{eq} is the equilibrium concentration. In terms of the propagation of the reaction interface position dr_c in a time interval dt, the mass flux of water is given by:

$$J_{H_2O} = -c_0 \frac{dr_c}{dt} \tag{3}$$

where r_c is the interface position. Combining Eq. 2 and Eq. 3, we have:

$$\frac{dr_c}{dt} = -\frac{k_r}{c_0}(1 - \frac{c_c}{c_{eq}}) , \quad r = r_c \tag{4}$$

As the particle is dehydrated, the core of the fully hydrated material (α phase) shrinks. The concentration distribution $c(r)$ of water in the β phase is governed by Fick's second law:

$$r^2 \frac{\partial c}{\partial t} = D_e \frac{\partial}{\partial r}(r^2 \frac{\partial c}{\partial r}) , \quad r_c \leq r \leq r_0 \tag{5}$$

where r is the spatial variable and D_e is the effective diffusivity of water through the porous β phase.

In order to preserve the mass balance at the interface, the mass flux relative to the moving interface must be considered. The amount of water generated from the interfacial reaction must be equal to the amount transported away from the interface. In particular, mass flux of convection must be converted from a fixed frame to the moving interface with an absolute velocity dr_c / dt. So the boundary condition at the moving interface is given as:

$$k_r(1 - \frac{c_c}{c_{eq}}) = -D_e \frac{\partial c(r,t)}{\partial r}\bigg|_{r=r_c} - \frac{dr_c}{dt} c_c , \quad r = r_c \tag{6}$$

Replacing dr_c / dt and rearranging the equation, the boundary condition at the interface can be rewritten as:

$$\left.\frac{\partial c(\mathrm{r,t})}{\partial r}\right|_{r=r_c} = -\frac{k_r}{D_e}(1-\frac{c_c}{c_{eq}})(1-\frac{c_c}{c_0}), \quad r=r_c \tag{7}$$

The boundary condition at the outer surface of the particle is given as:

$$c(\mathrm{r,t})=c_g, \quad r=r_0 \tag{8}$$

where c_g is the water concentration in the environment.

For the model to be as general as possible, the following nondimensional spatial and temporal variables are defined:

$$\hat{r}=\frac{r}{r_0}; \hat{t}=\frac{D_e t}{r_0^2}; \hat{c}=\frac{c-c_g}{c_{eq}-c_g}; \hat{r}_c=\frac{r_c}{r_0}$$

The corresponding dimensionless forms of the above equations are:

$$\frac{dr_c}{dt}=-Da\lambda(1-c_c), \quad r=r_c \tag{9}$$

$$r^2\frac{\partial c}{\partial t}=\frac{\partial}{\partial r}(\mathrm{r}^2\frac{\partial c}{\partial r}), \quad r_c \leq r \leq 1 \tag{10}$$

with boundary conditions

$$\left.\frac{\partial c(\mathrm{r,t})}{\partial r}\right|_{r=r_c} = -Da\lambda(1-c_c)(\mathrm{M}-c_c), \quad r=r_c \tag{11}$$

$$c(\mathrm{r,t})=0, \quad r=1 \tag{12}$$

where the hats are dropped for convenience, $\lambda=(c_{eq}-c_g)/c_{eq}$, $M=(c_0-c_g)/(c_{eq}-c_g)$ and $Da=(k_r r_0)/(D_e c_0)$ is the Damköhler number expressing the ratio of the chemical reaction rate to the mass transport rate.

The present model is solved by numerical scheme proposed by Illingworth and Golosnoy (Illingworth and Golosnoy 2005). The solution is based on the finite difference method with fully implict formulation. The moving interface is tracked by a variable grid method using a Landau transformation so that the moving interface is fixed at a grid point. A considerable advantage of this scheme is that finite difference equations are derived in such a way that mass conservation during the calculation is ensured.

RESULTS AND DISCUSSIONS

In this section, the shrinking core model is solved for a spherical particle for various values of the Damköhler number. It is worth noting that in all calculations, only the reaction rate constant k_r is tuned in order to achieve a range of Da values. The water concentration profile

as a function of dimensionless time for various *Da* values is shown in Fig. 2. Each profile shows the water content in the β phase from the moving interface to the particle surface. The arrow in Fig. 2 indicates the direction of propagation of the sharp interface between α/β phases. The shape of each profile at a certain time level is attributed to the interaction between the intrinsic reaction and the mass diffusion. From the definition of the Damköhler number, a small *Da* value means that the interfacial chemical reaction rate is relatively low compared to the diffusion rate of water molecules in the β layer. In the case of *Da* = 0.1, the interface moves very slow compared to the diffusion of water in the crystal. As a result, water released by reaction at the interface has sufficient time to drain away. In contrast, for a large *Da* value, e.g. *Da* = 100, the intrinsic chemical reaction is faster, and water cannot escape from the particle quickly enough. This leads to an increase of the water concentration near the interface, which in turn diminishes the propagation of the reaction interface. In other words, the Damköhler number plays a significant role in determining the nature of the diffusion/reaction dynamics. A very small *Da* value means that the overall reaction is controlled by the intrinsic chemical reaction at the interface, while a very large *Da* value means that the overall reaction is controlled by the diffusion of water through the β phase.
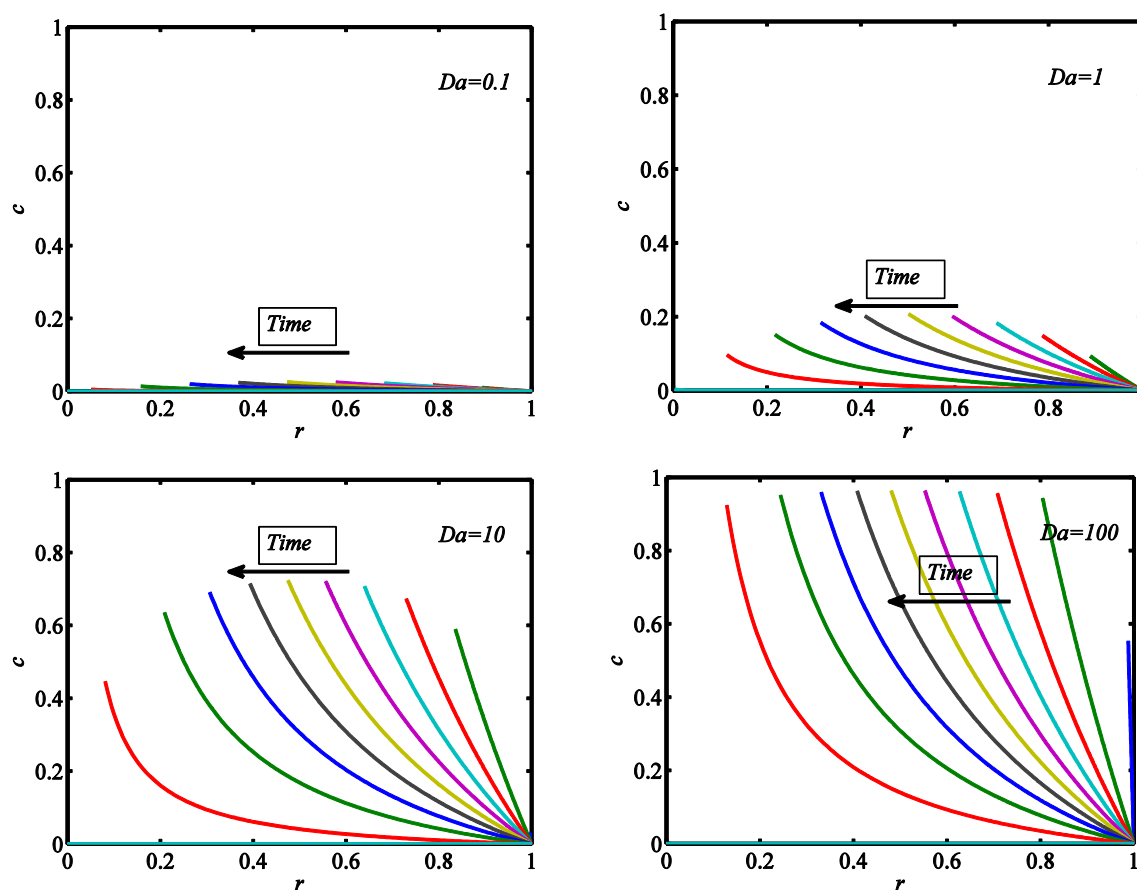
Figure 2: Profiles of water concentration distribution in a spherical particle for various Da values.

Another remarkable feature in the present results is that the water concentration at the interface decreases after it reaches a peak. The explanation is that as a structural model, the rate of reaction is essentially related to the reaction area which changes during the course of transforming the spherical particle. As the reactive area shrinks, the mass production at the interface also declines. As a result, a large percentage of gaseous water can diffuse away from

the particle during the same time period, which in return will accelerate the chemical reaction at the interface.

To further investigate the limiting mechanism of the reaction kinetics between the intrinsic reaction and the bulk diffusion process, the dimensionless interface position and normalized dimensionless interface velocity as a function of dimensionless time for the different values of *Da* are plotted in Fig. 3. At low values of *Da*, the interface position in Fig. 3(a) exhibits a linear dependence on time, which is consistent with the zero-order kinetics model used in the intrinsic reaction. In contrast, at high values of *Da* the process is diffusion controlled, where the plot of the interface position against time is curved.
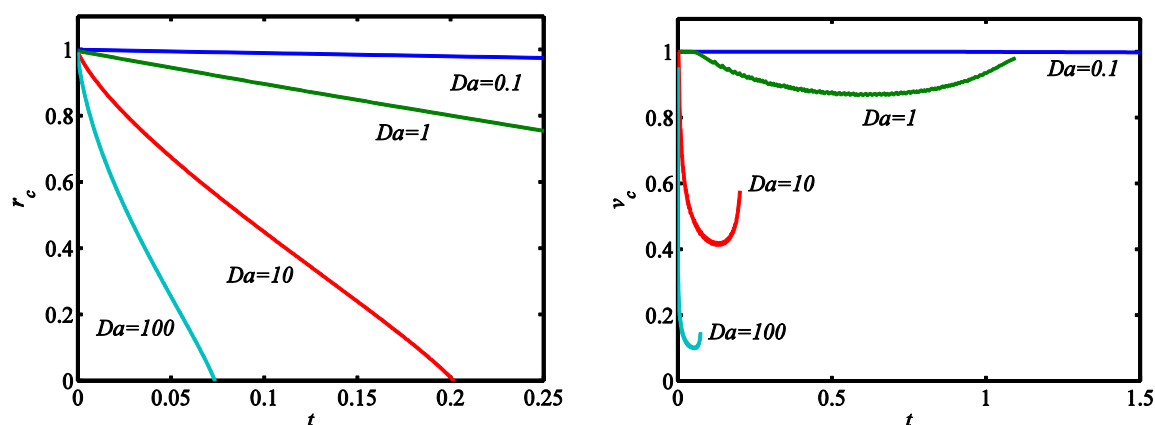

Figure 3: (a) Dimensionless interface position for various Da values; (b) Dimensionless interface velocity for various Da values (right).

In Fig. 3(b), the normalized dimensionless interface velocity is shown, which is defined by: $v_c = -\dfrac{1}{Da\lambda}\dfrac{dr_c}{dt} = 1 - c_c$. As discussed above, the velocity is constant at a small *Da* value corresponding to a linear r_c profile. With the increase of the *Da* value, the dimensionless velocity decreases rapidly, which is attributed to the diffusion limitation. In the case of *Da* = 1, the transition from a reaction to a diffusion controlled process can be observed. The overall kinetics of the dehydration reaction is initially controlled by the interfacial chemical reaction during which the interface velocity is constant. As the interface moves away from the particle surface, water vapor cannot diffuse out of the crystal efficiently, which leads to the accumulation of water molecules. Consequently, the movement of interface position is slown down gradually because the propagation of the reaction front is proportional to the difference of water concentration from the equilibrium concentration (see Eq. 4). The shape factor discussed above also explains the increase of the interface velocity in Fig. 3(b) after it reaches a minimum value. It is interesting to note that the interface velocity for *Da* = 1 almost increases to its initial value at the end of the reaction. The reaction kinetics will again be governed by the intrinsic reaction after it is governed by the intrinsic reaction in the initial stage of the dehydration process and by the mass diffusion during the second stage.

By integrating the water concentration, the fractional conversion of the salt hydrate can be plotted as a function of dimensionless time for different values of *Da*, see Fig. 4. Besides the numerical results at various *Da* values in solid lines, the line marked by '+' is the solution from the zero-order reaction model and the marked line by 'o' is the analytical solution of a pure diffusion process. As expected, our calculation results compare well with the theoretical analysis under the extreme cases in which either diffusion (large *Da*) or reaction (small *Da*)

dominates the dehydration process. In the case of $Da = 1$, the shape of fractional conversion is nearly linear as in the case of $Da = 0.1$. However, it is a result of the combined influence of interfacial reaction, mass diffusion and particle shape, instead of pure interfacial reaction as in $Da = 0.1$. Based on the previous discussion, it is safe to say that the range of Da values for which both intrinsic reaction and mass diffusion are important in determining the reaction kinetics is between 0.1 and 10, outside of which only a single mechanism, either the intrinsic reaction or the mass diffusion, is dominant in the reaction kinetics.
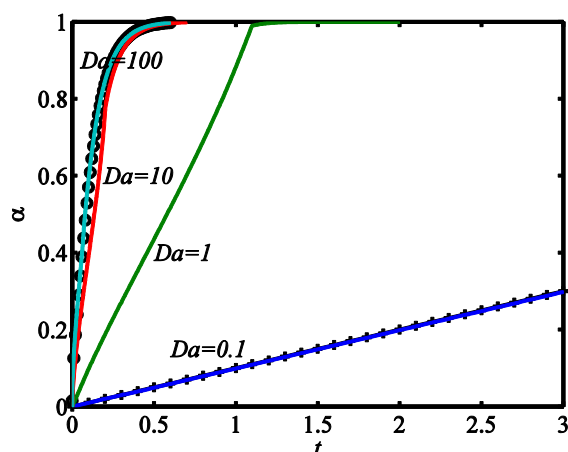

Figure 4: Fractional conversion as a function of dimensionless time for various values of Da during dehydration of a spherical particle. The marked lines by 'o' *and* '+' *are analytical solutions for pure diffusion and zero-order reaction, respectively.*

CONCLUSIONS

In this work a shrinking model is developed for describing the dehydration reaction of $Li_2SO_4.H_2O$ single particles. It includes the interaction between the intrinsic chemical reaction and the mass diffusion simultaneously. The Damköhler number is found to distinguish the controlling step during the transformation. A very small Da value means that the overall reaction is controlled by the intrinsic chemical reaction at the interface, while a very large Da value means that the overall reaction is controlled by the diffusion of water in the product phase. Fractional conversion calculated from the model agrees with the theoretical analysis under the extreme cases in which either diffusion (large Da) or reaction (small Da) dominates the dehydration process. Within the range of $Da = 0.1$ and $Da = 10$, both the intrinsic reaction and the mass diffusion are important in determining the reaction kinetics. In future work, experiments are designed to validate the model and to examine the dehydration reaction in a much more fundamental way. Information gained on the mechanisms of the dehydration reaction of $Li_2SO_4.H_2O$ monocrystals could form the basis for the development of a more rigorous kinetic model.

REFERENCES

C. Ferchaud, H. Zondag, R. d. Boer, C. Rindt, Characterization of the sorption process in thermochemical materials for seasonal solar heat storage application, in: Proceedings of the 12th International Conference on Energy Storage, Innostock, Lleida, Spain, 2012.
C. Schuh, Modeling gas diffusion into metals with a moving-boundary phase transformation, Metallurgical and Materials Transactions A 31 (10) (2000) 2411–2421.

I. Arvanitidis, S. Seetharaman, X. Xiao, Effect of heat and mass transfer on the thermal decomposition of $SrCO_3$ compacts, Metallurgical and Materials Transactions B 30 (5) (1999) 901–908.

M.E. Brown, A.K. Galwey, A.L.W. Po, Reliability of kinetic measurements for the thermal dehydration of lithium sulphate monohydrate.: Part 1. isothermal measurements of pressure of evolved water vapour, Thermochimica acta 203 (1992) 221–240.

M.E. Brown, A.K. Galwey, A.L.W. Po, Reliability of kinetic measurements for the thermal dehydration of lithium sulphate monohydrate.: Part 2. Thermogravimetry and differential scanning calorimetry, Thermochimica acta 220 (1993) 131–150.

P. Gupta, R.K. Saha, Mathematical modeling of noncatalytic fluid-solid reactions-generalized mathematical modeling of fluid-solid non-catalytic reactions using finite volume method: Nonisothermal analysis., Journal of chemical engineering of Japan 36 (11) (2003) 1298–1307.

R. Deshpande, Y.T. Cheng, M.W. Verbrugge, A. Timmons, Diffusion induced stresses and strain energy in a phase-transforming spherical electrode particle, Journal of the Electrochemical Society 158 (6) (2011) A718–A724.

S.B. Kanungo, S.K. Mishra, Thermal dehydration characteristics of hydrated salts: A critical review, Journal of the Indian Chemical Society 83 (2006) 1006-1017.

S. Yagi, D. Kunii, Studies on combustion of carbon particles in flames and fluidized beds, Symposium (International) on Combustion 5 (1) (1955) 231 – 244.

S. Yagi, D. Kunii, Fluidized-solids reactors with continuous solids feedi: Residence time of particles in fluidized beds, Chemical Engineering Science 16 (34) (1961) 364 – 371.

T.C. Illingworth, I.O. Golosnoy, Numerical solutions of diffusion-controlled moving boundary problems which conserve solute, Journal of Computational Physics 209 (2005) 207–225.

T. Knorr, M. Kaiser, F. Glenk, B.J. Etzold, Shrinking core like fluid solid reactionsa dispersion model accounting for fluid phase volume change and solid phase particle size distributions, Chemical Engineering Science 69 (1) (2012) 492–502.

T. Saetre, A model of hydrogen diffusion in spherical particles, International journal of hydrogen energy 31 (14) (2006) 2104–2111.

V.R. Subramanian, H.J. Ploehn, R. E. White, Shrinking core model for the discharge of a metal hydride electrode, Journal of the Electrochemical Society 147 (8) (2000) 2868–2873.

Z. Cui, F. Gao, J. Qu, Interface-reaction controlled diffusion in binary solids with applications to lithiation of silicon in lithium-ion batteries, Journal of the Mechanics and Physics of Solids 61 (2) (2013) 293–310.