

Chapter 2

Gas Diffusion Mechanisms and Models

2.1 Gas Diffusion in Porous Media

2.1.1 General Consideration

The one-dimensional diffusion of gas molecules in porous media involves molecular interactions between gas molecules as well as collisions between gas molecules and the porous media [1–3]. As gas fuel molecules travel through the porous media, one of three mechanisms can occur, depending on the characteristic of the diffusing gas species and the intrinsic microstructure of the porous media.³ The three mechanisms are molecular diffusion, viscous diffusion, and Knudsen diffusion. To distinguish among the three mechanisms, the Knudsen number (K_n), which is the ratio of the gas mean free path to the pore size of the electrode, is typically used, as shown in Eq. 2.1 [4]

$$K_n = \frac{\lambda}{d_p} \quad (2.1)$$

where d_p is the diameter of the pores, and λ is the gas mean free path, which can be calculated by Eq. 2.2,

$$\lambda = \frac{k_B T}{\sqrt{2} p \pi d_g^2} \quad (2.2)$$

where P is the gas pressure, d_g is the effective diameter of a gas molecule, k_B is the Boltzmann constant (1.3807×10^{-23} J/K), and T is the temperature of the gas (K). The effective molecular diameters can be estimated using the appropriate covalent and van der Waals radii, while the characteristic or equivalent pore diameter d_p should be evaluated based on the average pore size or chord length distribution [5–8].

If K_n is much greater than 10, collisions between gas molecules and the porous electrode are more dominant than the collisions between gas molecules, resulting in negligible molecular diffusion and viscous diffusion. If K_n is much smaller than 0.1, collisions and interactions between gas molecules become dominant, and

Knudsen diffusion becomes negligible compared with molecular diffusion and viscous diffusion. As K_n of a system ranges between 0.1 and 10, all three mechanisms govern gas transport. Different mathematical models have been developed to study the correlation among the parameters associated with the three different mechanisms, such as diffusion coefficient, gas flux, and gas concentration, among others [9, 10]. In this book, diffusion coefficient models are mainly employed.

2.1.2 Molecular Diffusion

Molecular diffusion or continuum diffusion refers to the relative motion of different gas species; this mechanism governs the total diffusion process, as the mean free path of gas molecules is at least one order larger than the pore diameter of the porous media. Fick's law (FL) is the most popular approach to evaluate gas diffusion in clear fluids and gases (non-porous media) due to its simplicity. FL actually has two forms. Fick's first law describes the correlation between the diffusive flux of a gas component and the concentration gradient under steady-state conditions. Fick's second law relates the unsteady diffusive flux to concentration gradient. Fick's first law is depicted in Eq. 2.3 [11]

$$J_i = \frac{-D_i c_i \partial(\mu_i)}{RT \partial x} \quad (i = 1, 2, \dots, n) \quad (2.3)$$

where J_i is the flux of gas species i , D_i is the bulk diffusivity, R is gas constant, T is temperature, x is one-dimensional diffusion path, c_i is molar fraction of gas species i , and μ_i is the chemical potential of species i at a given state [12]. μ_i is the function of the concentration/density of the mass species and can be expressed by Eq. 2.4,

$$\mu_i = \mu_0 + RT \ln c_i \quad (2.4)$$

where μ_0 is the standard chemical potential of gas i under 1 atm and 1 mol/L.

Fick's second law of diffusion for clear fluids predicts the effects of the concentration change with time on diffusion mechanism, as given by Eq. 2.5.

$$\frac{\partial c_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial x^2} \quad (2.5)$$

Since we mainly focus on the steady state of SOFCs under continuous operation, Fick's second law will not be discussed in the following section.

The above forms of FL are appropriate for clear fluids or gases. For application in porous media, Fick's first law is often modified by the introduction of a porous media factors, as shown in Eq. 2.6,

$$D_{ij}^{\text{eff}} = \frac{\phi}{\tau} D_{ij} \quad (2.6)$$

where D_{ij} is the binary diffusivity of gas species 1 and 2, D_{ij}^{eff} is the effective binary diffusivity of gas species 1 and 2, and ϕ and τ are the porosity and

Table 2.1 Lennard-Jones potential parameters found from viscosities for the common gas species of fuel cells

Substances		σ (Å)	ε/k_B (K)
H ₂	Hydrogen	2.827	59.7
O ₂	Oxygen	3.467	106.7
N ₂	Nitrogen	3.789	71.4
H ₂ O	Water	2.641	809.1
CH ₄	Methane	3.758	148.6
Air	Air	3.711	78.6
CH ₃ OH	Methanol	3.626	481.8
C ₂ H ₅ OH	Ethanol	4.530	362.6

Source Data from [15]

tortuosity of the porous media, respectively. The binary diffusivity D_{ij} can be estimated from the Chapman–Enskog theory, as shown in Eq. 2.7 [13]

$$D_{ij} = \frac{0.00186T^{\frac{3}{2}}}{p\sigma_{ij}^2\Omega} \left(\frac{1}{M_i} + \frac{1}{M_j} \right)^{\frac{1}{2}} \quad (2.7)$$

where D_{ij} is the diffusion coefficient measured in cm²/s, T is the absolute temperature in Kelvin, p is the pressure in atmospheres, and M_i are the molecular weights. The quantities σ_{ij} and Ω are molecular property characteristics of the detailed theory [14]. The collision diameter σ_{ij} given in angstroms is the arithmetic average of the two species as shown in Eq. 2.8.

$$\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j) \quad (2.8)$$

The dimensionless quantity Ω is more complex, but typically on the order of 1. Its detailed calculation depends on the integration of the interaction between the two species. This interaction is most frequently described by the Lennard-Jones potential (in 12–6 form). The resulting integral varies with the temperature and the interaction energy. This energy ε_{ij} is the geometric average of contributions from the two species given in Eq. 2.9.

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j} \quad (2.9)$$

Values of the ε/k_B are given in Table 2.1. Once ε_{ij} as a function of $k_B T/\varepsilon_{ij}$ is known, Ω can be calculated using the values in Table 2.2. The calculation of the diffusivities now becomes straightforward as σ_i and ε_i are known.

2.1.3 Knudsen Diffusion

As discussed earlier in this book, when the mean free path of gas molecules is on the same order as the tube dimensions, free-molecule diffusion (i.e. Knudsen diffusion) becomes important. Due to the influence of walls, Knudsen diffusion

Table 2.2 The collision integral Ω with respect to $k_B T / \varepsilon_{ij}$

$k_B T / \varepsilon_{ij}$	Ω	$k_B T / \varepsilon_{ij}$	Ω	$k_B T / \varepsilon_{ij}$	Ω
0.30	2.662	1.65	1.153	4.0	0.8836
0.40	2.318	1.75	1.128	4.2	0.8740
0.50	2.066	1.85	1.105	4.4	0.8652
0.60	1.877	1.95	1.084	4.6	0.8568
0.70	1.729	2.1	1.057	4.8	0.8492
0.80	1.612	2.3	1.026	5.0	0.8422
0.90	1.517	2.5	0.9996	7	0.7896
1.00	1.439	2.7	0.9770	9	0.7556
1.10	1.375	2.9	0.9576	20	0.6640
1.30	1.273	3.3	0.9256	60	0.5596
1.50	1.198	3.7	0.8998	100	0.5130
1.60	1.167	3.9	0.8888	300	0.4360

Source Data from [15]

includes the effect of the porous medium. The molecular flux of gas i due to Knudsen diffusion is given by the general diffusion equation (Eq. 2.10), [16]

$$J_{iK} = -D_{iK} \frac{\partial c_i}{\partial x} \quad (2.10)$$

where D_{iK} is the Knudsen diffusivity. The Knudsen diffusivity of gas species i can be estimated in Eq. 2.11, [17]

$$D_{iK} = \frac{d_p}{3} \sqrt{\frac{8RT}{\pi M_i}} \quad (2.11)$$

where M_i represents the molecular weights of gas species i , and d_p is the mean pore size of the porous media. D_{iK} can be simplified further as Eq. 2.12.

$$D_{iK} = 4850 d_p \sqrt{\frac{T}{M_i}} \quad (2.12)$$

In Eq. 2.12, d_p has the unit of cm, M_i has the unit of g/mol, and temperature T has the unit of K.

We can compare D_{iK} with the binary gas phase diffusivity, D_{ij} . First, D_{iK} is not a function of absolute pressure p or of the presence of species B in the binary gas mixture. Second, the temperature dependence for the Knudsen diffusivity is $D_{iK} \propto T^{1/2}$ versus $D_{ij} \propto T^{3/2}$ for the binary gas phase diffusivity.

Generally, the Knudsen process is significant only at low pressures and small pore diameters. However, instances exist where both Knudsen diffusion and molecular diffusion (D_{ij}) are important. If we consider that Knudsen diffusion and molecular diffusion compete with one another by a ‘‘resistances in series’’ approach, then the total diffusivity of species i in a binary mixture of i and j , D_i^t , is determined by Eq. 2.13. [18]

$$\frac{1}{D'_i} \cong \frac{1}{D_{ij}} + \frac{1}{D_{iK}} \tag{2.13}$$

The above relationships for the effective diffusion coefficient are based on diffusion within straight and cylindrical pores aligned in a parallel array. However, in most porous materials, pores of various diameters are twisted and interconnected with one another, and the path for diffusion of the gas molecules within the pores is “tortuous.” For these materials, if an average pore diameter is assumed, reasonable approximation for the effective diffusion coefficient in random pores is given by Eq. 2.14.

$$D_i^{t,eff} = \frac{\phi}{\tau} D'_i \tag{2.14}$$

The four possible types of pore diffusion are illustrated in Fig. 2.1, with each featured with their respective diffusivity correlation. The first three, pure molecular diffusion, pure Knudsen diffusion, and Knudsen and molecular combined diffusion, are based on diffusion within straight and cylindrical pores that are aligned in parallel array. The fourth involves diffusion via “tortuous paths” that exist within the compacted solid.

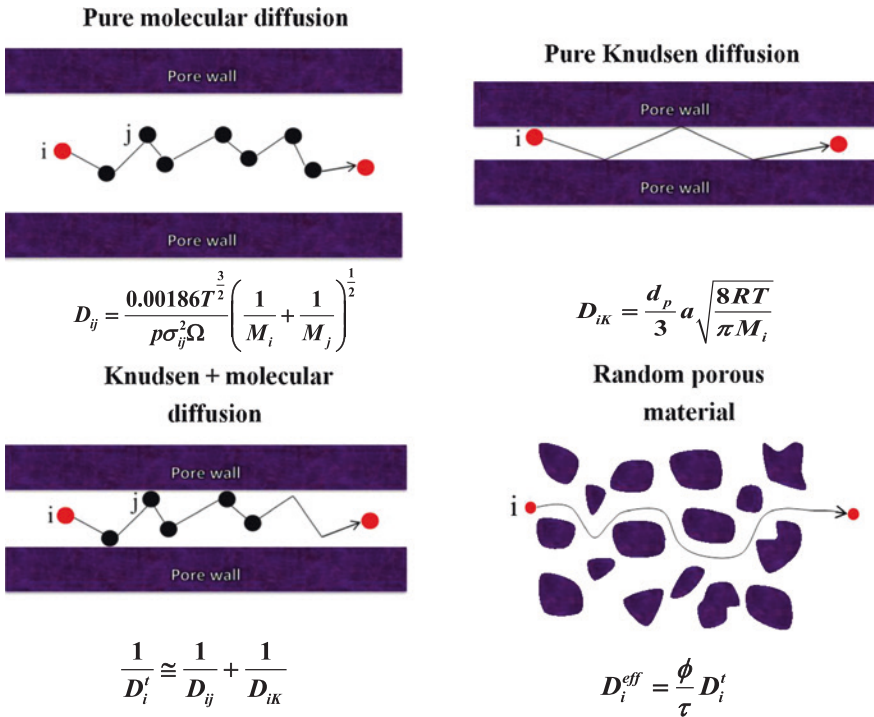


Fig. 2.1 Types of porous diffusion. Shaded areas represent non-porous solids. Adopted from Ref. [19]

2.2 Gas Diffusion in Porous Electrodes of Solid Oxide Fuel Cells

2.2.1 Advective–Diffusive Model

In SOFC systems, the electrode pores vary from a few nanometers to several micrometers in size, while the mean free path of fuel gas molecules is a few hundred nanometers. Therefore, K_n is in the range of 0.1–5, and all the three gas transport mechanisms must be considered. Further, the different models must be comprehended to understand the gas transport of a typical SOFC system. Different theoretical models have been proposed to describe the gas transport of SOFC systems. Owing to its inherent simplicity, FL has been most widely employed diffusion-based model. FL considers only molecular diffusion and assumes that the gas flux is proportional to gas pressure gradient. This drawback is addressed in the extended FL model, which combines molecular diffusion modeled by FL and viscous diffusion modeled by Darcy's law. The extended FL, also known as an advective–diffusive model (ADM), is expressed in Eq. 2.15,

$$J_i = -\frac{k_i}{\mu_g} \rho_g \omega_i \nabla p_t - D_{ij} \rho_g \nabla \omega_i \quad (2.15)$$

where k_i is effective permeability, μ_g is gas viscosity, ρ_g is gas density, D_{ij} is binary gas diffusivity, ω_i is mass fraction of gas species i , and P_t is total gas pressure [20].

2.2.2 Maxwell–Stefan Model

Both FL and ADM only take into account unidirectional interactions in simple dilute binary gas systems; neither of them is valid for ternary or concentrated gas systems where molecular interactions cannot be neglected. To model such complicated systems, the Maxwell–Stefan model (MSM) was developed, which is shown in Eqs. 2.16–2.17,

$$\frac{dX_i}{dz} = \sum_{j=1}^n \frac{X_i J_j - X_j J_i}{c D_{ij}}, \quad i = 1, 2, \dots, n \quad (2.16)$$

$$\frac{dX_i}{dz} = \sum_{j=1}^n \frac{X_i J_j - X_j J_i}{c D_{ij}^{\text{eff}}}, \quad i = 1, 2, \dots, n \quad (2.17)$$

where X_i is the mole fraction of gas species i , c is total concentration, D_{ij} is Maxwell–Stefan diffusivity, J_i is molar flux of gas species i , and D_{ij}^{eff} is effective gas diffusivity [21]. MSM can model the gas transport in uniform media or in electrostatic fields.

2.2.3 Dusty Gas Model

MSM fails to model gas systems where gas species frequently collide with the porous media. To model such gas systems accurately, a dusty gas model (DGM) was developed, which is shown in Eqs. 2.18–2.19,

$$\sum_{j=1, j \neq i}^n \frac{X_i J_j^D - X_j J_i^D}{D_{ij}} - \frac{J_i^D}{D_{iK}} = \frac{p_t \nabla X_i}{RT} + \frac{X_i \nabla p_t}{RT} \quad (2.18)$$

$$\sum_{j=1, j \neq i}^n \frac{X_i J_j^T - X_j J_i^T}{D_{ij}} - \frac{J_i^T}{D_{iK}} = \frac{p_t \nabla X_i}{RT} + \left(1 + \frac{k_0 p_t}{D_{iK} \mu_g}\right) \frac{X_i \nabla p_t}{RT} \quad (2.19)$$

where X_i is gas mole fraction, J_j^D is diffusive molar flux of gas species j , J_j^T is total diffusive and advective molar flux, P_t is total gas pressure, R is gas constant, T is temperature, D_{ij} is binary diffusivity in free space, D_{iK} is Knudsen diffusivity of gas species i , and k_0 is the gas permeability [22]. The DGM considers all possible interactions and collisions and exhibits high accuracy while modeling gas fuel transport through porous fuel cell electrodes. However, DGM has not been as widely used as FL due to the complexity in modeling multicomponent gas fuel systems. The accuracy of DGM coupled with the simplicity of FL yielded the recently developed DGM-FL, which is a more practical gas diffusion model. The model is expressed in Eq. 2.20,

$$J_i = J_i^{\text{diffusion}} + J_i^{\text{convection}} = -\bar{D}_2 \nabla \bar{c}_2 - \bar{c}_2 \frac{\bar{k}_2}{\mu} \nabla p_t \quad (2.20)$$

where \bar{D}_2 , \bar{c}_2 , and \bar{k}_2 are simplified diffusivity, molar concentration, and permeability of gas species, μ is chemical potential, and P_t is total gas pressure [23]. DGM-FL was obtained by deriving DGM in FL form. This approach results in a simple, efficient, and reliable model of a typical gas transport system. To account for both Knudsen and viscous effects simultaneously, a binary friction model (BFM) was derived, as shown in Eq. 2.21,

$$\frac{dp}{dx} = -RTN \left(D_{iK}^{\text{eff}} + \frac{k_0 P}{\mu_g} \right)^{-1} \quad (2.21)$$

where P is gas pressure, N is net gas transport, D_{iK}^{eff} is Knudsen diffusivity, k_0 is the gas permeability, and μ_g is the viscosity of the gas species [24, 25]. Compared to Darcy's law that only takes viscous effects into account, BFM shows improved accuracy as it is employed to model gas transport phenomena in fuel cells [26].

2.2.4 Effective Gas Diffusion Model

In the discussed models, the term “effective gas diffusivity” was mentioned. We need to look into multicomponent diffusion to comprehend the term in more details. Effective binary gas diffusivity was developed to simplify computations on the diffusion parameters of a multicomponent gas system since the diffusion fluxes in a fuel cell system are often required at various locations and time points [27–29]. In the effective binary diffusion, a multicomponent gas system is approximated as a binary mixture of gas species i and a composite gas species corresponding to all the other gas species in the system. By introducing effective binary gas diffusivity, any multicomponent gas system can be conveniently treated as a binary gas system. As molecular diffusion, viscous diffusion, and Knudsen diffusion are all considered, the flux of an isothermal binary gas system, such as O_2/N_2 and H_2/H_2O , can be modeled by Eqs. 2.22–2.23 [18]

$$J_1 = -D_1^{t,eff} \nabla c_1 + X_1 \delta_1 J - X_1 \gamma_1 \left(\frac{ck_0}{\mu} \right) \nabla p_t \quad (2.22)$$

$$J_2 = -D_2^{t,eff} \nabla c_2 + X_2 \delta_2 J - X_2 \gamma_2 \left(\frac{ck_0}{\mu} \right) \nabla p_t \quad (2.23)$$

where

$$\delta_1 = 1 - \gamma_1 = \frac{D_{1K}^{eff}}{D_{1K}^{eff} + D_{12}^{eff}} \quad \text{and} \quad \delta_2 = 1 - \gamma_1 = \frac{D_{2K}^{eff}}{D_{2K}^{eff} + D_{12}^{eff}} \quad (2.24)$$

$$\frac{1}{D_1^{t,eff}} = \frac{1}{D_{1K}^{eff}} + \frac{1}{D_{12}^{eff}} \quad \text{and} \quad \frac{1}{D_2^{t,eff}} = \frac{1}{D_{2K}^{eff}} + \frac{1}{D_{12}^{eff}} \quad (2.25)$$

In Eqs. 2.24–2.25, J_1 and J_2 are the fluxes of gas species 1 and 2, J is the total flux, c_1 and c_2 are the concentrations of gas species 1 and 2, c is the total gas concentration, X_1 and X_2 are the molar fractions of gas species 1 and 2, μ is viscosity, k_0 is the gas permeability, P_t is total pressure, D_{iK}^{eff} and D_{2K}^{eff} are the effective Knudsen diffusivities of gas species 1 and 2, and D_{12}^{eff} is the effective binary diffusivity.

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