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Overview of Molecule and Ion Transport Through Polymer Membranes

Energy and environmental issues have become increasingly important on a global scale, as they are often interconnected. For example, hydrogen fuel cells, which generate electricity with minimal CO_2 emissions, offer an energy-efficient solution that addresses both environmental and energy concerns. To tackle these challenges, industries such as electrochemical energy conversion and storage as well as petrochemicals are focusing on more energy-efficient processes to generate fuels such as hydrogen. Among the key technologies supporting these efforts is membrane-based separation, which plays a growing key role in both academic research and industrial applications.

Membrane technologies enable the selective transport of molecules and ions through different mechanisms based on the pore size of the polymeric membrane, as shown in Figure 1.1 [1]. When pores are large, the transport of molecules, for instance, follows Newtonian flow, while smaller pores lead to Knudsen flow or molecular sieving. In nonporous membranes, the solution–diffusion mechanism dominates (Figure 1.1d). This book will focus specifically on diffusional transport of small molecules – gases, vapors, and liquids – and ions, through nonporous polymer membranes based on the solution-diffusion mechanism.

A solid understanding of molecule and ion transport through polymer membranes is essential for designing efficient materials and optimizing their performance. The

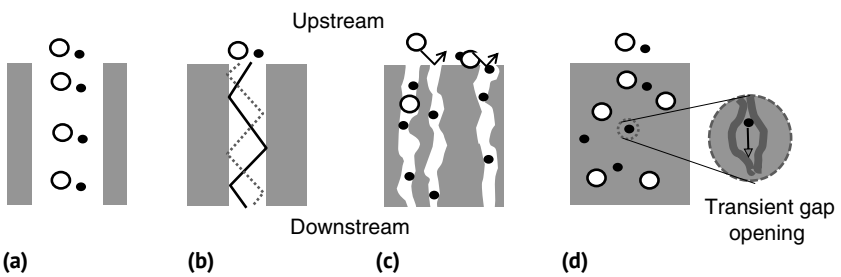

Figure 1.1 Schematic representation of main mechanisms of membrane-based separations: (a) Newtonian flow; (b) Knudsen flow with pore 2–50 nm; (c) sieving mechanism with pore <0.7 nm; and (d) solution–diffusion mechanism without pore. *Source*: Adapted from [1].

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solution–diffusion model is represented by Fick's law for molecule transport and additional Ohm's law for ion transport, both of which describe how diffusional flux is driven by concentration and electric potential gradients, respectively. Since polymer membranes are widely used in separation processes, understanding these transport mechanisms is crucial for improving membrane efficiency in various applications. This book starts with the "Introduction to Polymeric Materials" and then continues with two parts containing "Molecule Transport Through Polymer Membranes" and "Ion Transport Through Polymer Membranes." Thus, in this chapter, similarities and differences between molecule and ion transport will be briefly addressed first, followed by overviews of the two parts.

1.1 Molecule Transport

Diffusional transport of molecules can be readily visualized by dropping a black ink droplet into water without any convectional flow. Black-colored ink spreads out through water three-dimensionally by diffusion process (Figure 1.2a). Mass transport through polymeric materials is also evidenced by air transport, both oxygen and nitrogen, through a balloon wall made of rubbery polymers. When a balloon is blown to expand its size with a higher pressure (p_{in}) than the outer atmospheric pressure (p_{out}) at time zero, the balloon after a certain time (hours) will be shrunk into a smaller or crushed shape because of the mass (oxygen and nitrogen) transport across the balloon wall (Figure 1.2b).

Adolph Fick in 1855 wrote that "The transfer of salt and water occurring in a unit of time, between two elements of space filled with differently concentrated solutions of the same salt, must be, *caeteris paribus*, directly proportional to the difference of concentration, and inversely proportional to the distance of the elements from one another." In mathematical language, this may be thus expressed as [2]:

$$J_j = -D_j \frac{\mathrm{d}c_j}{\mathrm{d}x} \tag{1.1}$$

where one-dimensional molar flux J_j (mol/cm^{2}sec) for x (cm) direction is proportional to the concentration gradient $\mathrm{d}c_j/\mathrm{d}x$ (mol/cm^{3}cm) of species j, and the proportionality constant D_j (cm^2/sec) is called diffusion coefficient [2, 3]. Equation (1.1), commonly called as the Fick's first law, has been conveniently used to describe the diffusional mass transport.

In the case of gases, the pressure gradient $\mathrm{d}p_j/\mathrm{d}x$ is frequently used rather than the concentration one, mostly for convenience:

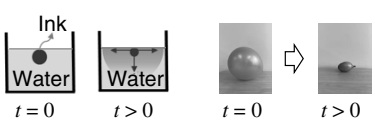

Figure 1.2 Schematics for (a) diffusion of black-colored ink in water and (b) photographs for air transport across the balloon wall with time because $p_{in} > p_{out}$. *Source*: Y.S. Kang.

$$J_j = -P_j \frac{\mathrm{d}p_j}{\mathrm{d}x} \tag{1.2}$$

Here, P_j is called the permeability or permeation coefficient, defined as a product of the diffusion coefficient D_j and the solubility coefficient S_j: $P_j = D_j \times S_j$. The more detailed explanation is available in Section 3.1 of Chapter 3.

However, mass flux is more rigorously expressed by the chemical potential gradient, $\mathrm{d}\mu_j/\mathrm{d}x$, rather than the concentration gradient, $\mathrm{d}c_j/\mathrm{d}x$. The chemical potential, μ_j, is given by $\mu_j = \mu_j^0 + RT \ln a_j$, where a_j is the chemical activity, defined as $a_j = \gamma_j c_j$ with γ_j being the activity coefficient and μ_j^0 is the standard chemical potential at $a_j = 1$.

Under ideal conditions with the activity coefficient $\gamma_j = 1$, $\mathrm{d}\mu_j/\mathrm{d}x$ is directly related with $\mathrm{d}c_j/\mathrm{d}x$ as:

$$\frac{\mathrm{d}\mu_j}{\mathrm{d}x} = \frac{RT}{c_j}\frac{\mathrm{d}c_j}{\mathrm{d}x} \tag{1.3}$$

Substituting Equation (1.3) into (1.1) gives:

$$J_j = -\left(\frac{D_j c_j}{RT}\right)\frac{\mathrm{d}\mu_j}{\mathrm{d}x} \tag{1.4}$$

Therefore, Equation (1.4) is another expression of Fick's law in terms of chemical potential gradient.

1.2 Ion Transport

Ion possesses electrical charge in addition to its mass. Therefore, driving forces for ion transport involve two different modes: one for mass and the other for charge. The former is chemical potential gradient, as described previously, and the latter is the electric potential gradient. Therefore, the total driving force can be expressed as electrochemical potential gradient, where it is summation of chemical potential gradient and electrical potential gradient.

Electrochemical potential $\bar{\mu}_j$ is the total energy required to move a charged particle (like an ion or electron) from one point to another, combining both its chemical potential μ_j (J/mol) (related to concentration) and the electrical potential φ (V = J/C) (related to charge), which is mathematically expressed as:

$$\bar{\mu}_j = \mu_j + z_j F \varphi \tag{1.5}$$

where the charge number z_j is positive for cation and negative for anion, and F (C/mol) is the Faraday constant.

Then, the electrochemical potential gradient $\bar{\mu}_j/\mathrm{d}x$ can be readily obtained from Equations (1.3) and (1.5) as:

$$\frac{\mathrm{d}\bar{\mu}_j}{\mathrm{d}x} = RT\left(\frac{1}{c_j}\frac{\mathrm{d}c_j}{\mathrm{d}x} + \frac{z_j F}{RT}\frac{\mathrm{d}\varphi}{\mathrm{d}x}\right) \tag{1.6}$$

Replacing the chemical potential gradient $d\mu_j/dx$ in Equation (1.4) with electrochemical potential gradient $\bar{\mu}_j/dx$ of Equation (1.6) yields:

$$J_j = -D_j c_j \left(\frac{1}{c_j} \frac{dc_j}{dx} + \frac{z_j F}{RT} \frac{d\varphi}{dx} \right) \tag{1.7}$$

Equation (1.7) is called the Nernst–Planck electrodiffusion equation contributed from two different transport mechanisms (the first term for diffusion and the second for migration), which will be explained in more detail in Section 8.5 of Chapter 8.

Electron transport across an electronic conductor can be conveniently described by Ohm's law. It says that the electric current I (A) is linearly proportional to applied voltage V (V) and inversely proportional to resistance R (Ω): $I = V/R$, which can be rearranged to:

$$j = -\sigma \frac{d\varphi}{dx} \tag{1.8}$$

where j (A/cm^2 = C/cm^{2}sec) is the current density, $d\varphi/dx$ is the electric potential gradient and σ (S/cm = 1/Ω cm) is the conductivity.

Equation (1.8) can be applied to the ion transport associated with the electrochemical potential gradient because the ion contains charges in addition to mass. In real electrolyte solutions containing salts dissolved in a solvent, mass transport always accompanies the charge transport because every ion in the electrolyte has its own charge. Therefore, there will be two different ion transport modes: diffusion due to the concentration gradient and migration or drift due to the electric potential gradient. Such differences must be always recognized as long as you deal with the ion transport.

1.3 Similarities and Differences Between Molecule and Ion Transport

Free volume theory and facilitated transport phenomena help explain how both molecules and ions transport through solid-state polymers, although their driving forces are different. For ion transport, overall electroneutrality should be macroscopically met in any electrochemical devices. This section briefly introduces the key concepts to transport in polymers, including free volume theory, facilitated transport, diffusion, migration, transport parameters, and electroneutrality.

1.3.1 Free Volume Theory

When a molecule dissolved in a polymer finds an empty space or free volume in a polymer matrix, it can move from one position to another by diffusional jump due to its thermal motion at a given temperature. In this case, diffusion process can be determined by the diffusional jump distance δ and also by the jump frequency ϕ, which are mostly determined by the amount of the free volume and its size, as shown in Figure 1.3a.

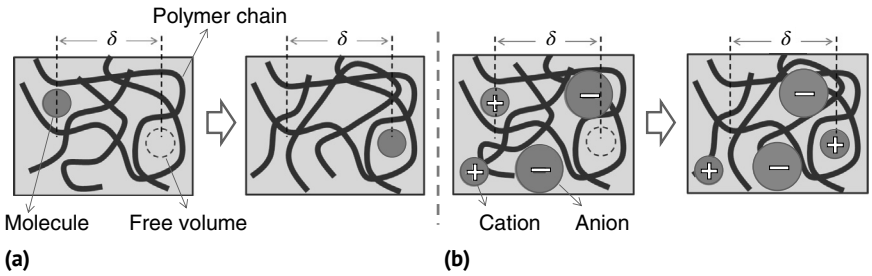

Figure 1.3 Schematic drawings of diffusional jump with distance δ of (a) molecule and (b) ion through free volume or empty space among polymer chains. *Source*: Y.S. Kang.

The direct relationship between the diffusion coefficient and the amount of the free volume in a given polymer has been observed. One of the most popular models is the free volume theory, suggesting that the diffusion coefficient D exponentially increases with the amount of free volume or the size of the free volume:

$$D = D_0 \exp\left(-\frac{B_d}{f}\right) \tag{1.9}$$

where f is the fractional free volume (FFV) defined as $f = V_F/V$ with V_F and V being the total specific free volume and the specific volume, respectively. B_d represents the minimum volume size required for diffusional jump, and D_0 is the pre-exponential factor. Since no extra energy is assumed to be necessary for redistribution of the free volume in a liquid-like matrix, it works well with most rubbery polymers because of their high chain mobility. Surprisingly, it also works well even common glassy polymers where free volume redistribution would hardly occur because of their practically frozen chain mobility in glassy states.

The free volume theory can also be applied for ion transport through solid polymer electrolytes (SPEs) and ion exchange membranes (IEMs). This is because the basic concepts of the diffusional process for both molecule and ion transport are nearly equivalent to each other as schematically shown in Figure 1.3a and b. More detailed descriptions for diffusion of molecules and ions will be covered in Chapters 3 and 8, respectively, in this book. All these results suggest that the fundamental concepts of transport of (small and neutral) molecules and ions are nearly equivalent to each other according to the free volume theory.

1.3.2 Facilitated Transport in the Solid State

Another similarity between molecule and ion transport is the facilitated transport in the solid state in addition to the free volume theory. Facilitated transport was originally observed in liquid blood for oxygen transport from heart to organs in animals. However, facilitated transport in the solid state has been observed and intensively investigated recently, which will be described in detail in Chapter 4 of this book. The facilitated transport is the sum of the two different transport modes of the Fickian transport and carrier-mediated transport. The Fickian transport, governed by the solution–diffusion mechanism, is a mass transport caused by the concentration

gradient. The carrier-mediated transport occurs through the reversible interactions between a solute A and carrier C, where the carrier C is defined as any kind of chemical compound, which *selectively* and *reversibly* interacts the specific solute A from its mixture as:

$$A + C \underset{k_2}{\overset{k_1}{\rightleftarrows}} [A \cdot \cdot C] \qquad K = k_1/k_2 \tag{1.10}$$

where k_1 and k_2 are forward and backward reaction rate constants with equilibrium constant K. One characteristic feature of facilitated transport in the solid state is to simultaneously increase the flux of A, represented by its permeability, and the selectivity of A over the others, which are commonly in conflict among most polymers: high permeability with low selectivity and *vice versa*. Therefore, facilitated transport in the solid state has huge advantage to improve the separation performance markedly.

The first example of the facilitated molecule transport in the solid state is O_2 transport through a membrane containing Co(II) or Fe(II) coordinated in polymers, as shown in Figure 1.4a, resulting in the high permeability as well as high O_2/N_2 selectivity. Transport of olefins like ethylene and propylene is markedly increased by the olefin carrier action of silver ions Ag^+ dissolved in polymer to make polymer electrolytes (Figure 1.4b). Here, Ag^+ has selective and reversible interactions with only olefins, but not with paraffins like ethane and propane. As a result, the propylene permeability increases more than 100-fold with almost 500-fold increase in the propylene selectivity over propane through silver polymer electrolytes. These are representative examples of facilitated molecule transport in the solid state.

In the case of ion transport through SPEs and IEMs facilitated ion transport in the solid state has been frequently observed, which is not commonly termed as facilitated transport anyway. Here representative examples of facilitated ion transports in the solid state will be introduced. For instance, lithium salts like $LiCF_3SO_3$ are dissolved in a polymer matrix containing ligands of O, N, or S atoms to form polymer electrolyte. Then we can imagine the specific and reversible interactions between Li^+ and oxygen atoms in polymers like poly(ethylene oxide) for facilitated Li^+ transport in SPEs (Figure 1.5a). In IEMs like proton exchange membranes (PEMs) with microphase-separated structures containing ion channels with fixed charge group of sulfonate anions $—SO_3^-$ dispersed in hydrophobic polymer matrix, specific and reversible interactions between H^+ and $—SO_3^-$ at the interface of ion channels (Figure 1.5b), which facilitate the proton transport through the interfacial layer of the ion channels.

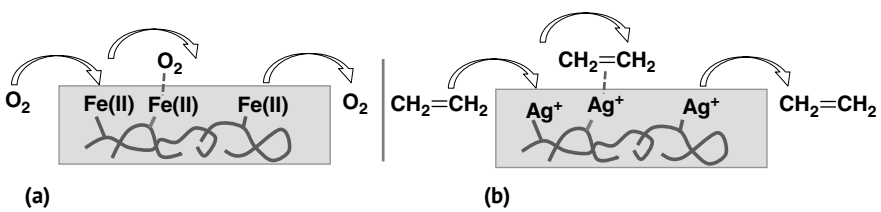

Figure 1.4 Schematic illustrations of facilitated transport in the solid state for (a) oxygen and (b) ethylene. (--) represents coordinative interaction. *Source*: Y.S. Kang.

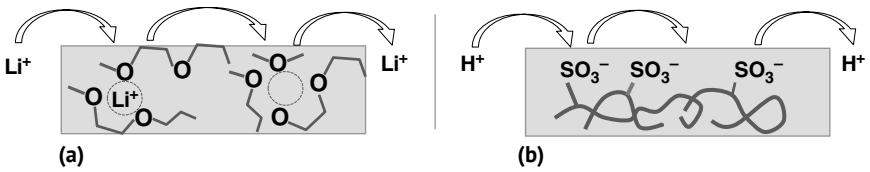

Figure 1.5 Schematic illustrations of facilitated transport in the solid state for (a) Li^+ in polymer electrolyte and (b) H^+ in cation exchange membrane. *Source*: Y.S. Kang.

Table 1.1 Characteristics and Differences of molecule transport and ion transport.

	Molecule transport	**Ion transport**
Transporting species	Molecules with mass only	Ions with mass and charge
Transport mechanism	Diffusion	Diffusion and migration (or drift)
Driving force	Chemical potential gradient (concentration gradient)	Electrochemical potential gradient (concentration and electric potential gradient)
Governing law	Fick's law	Fick's law and Ohm's law
Transport model	Free volume theory	Free volume theory
Facilitated transport	With carriers	With carriers
Constraint	No	Electroneutrality

Therefore, as a short summary, facilitated transport similarly prevails in both molecule and ion transport in the solid state because of the selective and reversible interactions of molecules and ions with their corresponding carriers.

1.3.3 Diffusion and Migration

Even though the transport mechanisms of molecules and ions are commonly described by the free volume theory, the fundamental difference between molecule and ion transports is due to the fact that ion has electric charge whereas molecule does not. Therefore, ion has two different transport modes or fluxes: diffusional flux j_d due to the concentration gradient, described by the Fick's law, and migrational flux j_m due to the electric potential gradient, described by Ohm's law. Therefore, it is anticipated that the directions of the diffusion and the migration are the same or opposite, depending on the voltage applied, as shown in Figure 1.6a and b. It is important to note here that the total current density j (C/cm^2 sec) is the vectorial summation of diffusion and migration: $j = j_d + j_m$, suggesting that j becomes either small or big depending on the directions of j_d and j_m. A summary of the characteristics and differences of molecule and ion transports is provided in Table 1.1.

1.3.4 Transport Parameters and Electroneutrality

Transport properties of gas in polymeric membranes are mostly characterized by diffusion coefficient D_j, solubility coefficient S_j, permeability P_j of molecular species j,

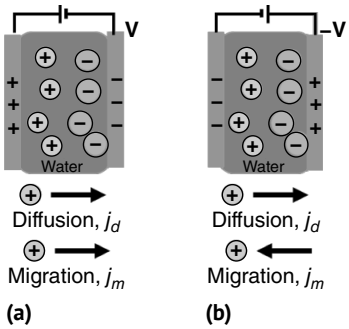

Figure 1.6 Schematic transport of cation under applied potential difference *V*: (a) co-current and (b) counter-current between diffusion and migration. *Source*: Y.S. Kang.

Table 1.2 Transport parameters for molecule transport and ion transport.

Molecule transport	Ion transport
Mass flux, J_j	Current density (charge flux), j_j
Permeability, P_j	Conductivity, σ
Diffusion coefficient, D_j	Diffusion coefficient, D_j
Mobility, u_j	Mobility, u_j
Selectivity, α_{ij}	Permselectivity, P_j^m
—	Transport number, T_j
—	Charge transfer resistance, R_{CT}
—	Ion exchange capacity, IEC

and their permeability ratio α_{ij} of molecular species i and j as a selectivity, whereas those of ion by conductivity σ, mobility u_j, permselectivity P_j^m, and transport number T_j. In addition, charge transport resistance R_{CT} and ion exchange capacity (IEC) also play important roles in determining charge transport in most SPEs and IEMs, respectively. Characteristics of molecule and ion transports are listed in Table 1.2.

1.4 Overview of Molecule and Ion Transport Through Polymer Membranes

This book is divided into two main parts: Part I focuses on molecule transport, while Part II explores ion transport through polymer membranes. In this context, "molecule" refers to uncharged, small-sized species such as gases or organic solvents. Since all materials discussed in this book are polymer-based, Chapter 2 briefly introduces the fundamentals of polymer materials.

1.4.1 Fundamentals on Polymeric Materials

A comprehensive understanding of polymeric materials forms the foundation for studying molecule and ion transports. Chapter 2 explores the interactions of polymer with small molecular solvents, including polymer solution and phase separation behavior. The former will be applied for the sorption behavior of organic vapors and liquid sorbents, while the latter for the formation of microphase-separated structures for asymmetrically microporous support of composite membranes.

The chapter then introduces the concepts of free volume and free volume theory, where the free volume refers to the unoccupied spaces within a polymer matrix that allow for molecules and ions to diffuse. The theory provides a framework for understanding how molecules and ions transport through these spaces and therefore offers insights into the relationship between polymer structure and transport properties.

The nonequilibrium features of glassy polymers and physical aging are also highlighted. Glassy polymers, being in a nonequilibrium state, undergo physical aging at sub-glass transition temperatures, leading to changes in free volume and transport properties and their relationship over time. Lastly, sub-glass transitions, such as the γ-relaxation, involve localized segmental motions that can influence diffusion processes.

Finally, the chapter briefly touches on the crystal structure, crystallization kinetics, and the viscoelastic and mechanical properties of polymers, rounding out the foundational knowledge needed for the study of molecule and ion transport.

1.4.2 Part 1: Molecule Transport Through Polymer Membranes

Understanding the fundamental principles governing molecule transport is essential for designing membranes with tailored properties. Part 1 (Chapters 3–7) of this book discusses both the theoretical and practical aspects of molecular diffusion, sorption, and permeation in polymer systems.

Chapter 3 introduces Fick's Law, a widely accepted solution–diffusion model essential for understanding how molecules permeate polymeric membranes. This model provides the basis for determining key parameters such as the diffusion coefficient, solubility coefficient, permeability, and selectivity. A detailed discussion of the free volume theory, including models proposed by Cohen–Turnbull, Fujita, and Vrentas–Duda, illustrates how molecular transport is influenced by the available free volume within polymer matrices. This chapter also emphasizes mathematical models for transient sorption and permeation through glassy polymers and composite membranes, offering a strong analytical basis for further study.

Chapter 4 builds on the facilitated transport phenomena in solid-state polymer membranes. It highlights various mathematical models, such as the dual transport model, effective diffusion model, limited chain mobility model, and concentration fluctuation model, which provide insights into how molecular transport can be facilitated by carrier-mediated processes. Special attention is given to oxygen, carbon dioxide, and olefin transport, where carriers like metallic ions, surface-activated nanoparticles, and ionic liquids play a pivotal role in improving transport efficiency.

Chapter 5 transitions into selective transport membranes, where the concepts of permeability and selectivity, mathematically defined here, play crucial roles in understanding separation performance. This part investigates the relationship between polymer structure and transport properties, categorized into polymers with flexible chains, stiff chains, and extremely stiff chains with high free volume. The role of physical aging and plasticization in glassy polymers is discussed, providing insights into how membrane performance can change over time.

Chapter 6 covers the measurement of key transport parameters, such as diffusion coefficient, solubility coefficient, and permeability. It provides detailed theoretical backgrounds and experimental methods, including manometric, gravimetric, and time-lag techniques, for assessing these transport properties. This chapter is critical for readers interested in practical methodologies for evaluating polymer membranes.

Chapter 7 introduces practical applications, including separations of hydrogen, oxygen/nitrogen, carbon dioxide, and olefin/paraffin, including propylene/propane and ethylene/ethane mixtures, offering real-world relevance for the theories and models covered in earlier chapters.

The chapters collectively provide a comprehensive overview of small neutral molecular transport through polymer membranes to offer a clear understanding of the challenges and opportunities in this field.

1.4.3 Part 2: Ion Transport Through Polymer Membranes

Part 2 (Chapters 8–12) of the book, titled *Ion Transport Through Polymer Membranes*, shifts the focus from small neutral molecules to charged species, examining the unique challenges and mechanisms involved in ion transport. Chapters 8–12 discuss the electrochemical fundamentals, polymer electrolytes, and IEMs that are pivotal for energy conversion and storage devices involving ion transport, such as secondary batteries, solar cells, fuel cells, and water-splitting applications.

Chapter 8 provides the necessary background in electrochemistry, focusing on key concepts of electrochemical potential and its influences on electrochemical reaction kinetics and ultimately ion transport. The ion transport mechanism, including diffusion and migration or drift due to the concentration gradient and electric potential gradient, respectively, is also introduced to provide insight into ion conductivity and transport number. This chapter also explores the electric double layer and how it impacts charge transfer and mass transport of ions, providing a theoretical basis for the subsequent chapters on polymer electrolytes and IEMs.

Chapter 9 delves into polymer electrolytes, which are essential for devices like secondary batteries and sensitized solar cells. It covers the formation of polymer electrolytes, the generation of free charge carriers, and the various mathematical models of ionic conduction, such as the free volume model, conformational entropy model, dynamic bond percolation (DBP) model, and Anderson and Stuart model. Additionally, it explores the role of temperature and glass transition in influencing polymer chain mobility, which directly affects ionic transport. Emerging polymer electrolytes, including polymer-in-salts (PISs) and nanocomposite structures, are discussed as promising materials for future energy storage applications.

Chapter 10 focuses on IEMs, including cation and anion exchange membranes (CEMs and AEMs), as well as bipolar membranes (BPMs). This chapter highlights the structure–property relationships that dictate conductivity and selectivity in IEMs. The concept of permselectivity is introduced to explain how these membranes differentiate between ions of the same charge. It also examines the formation of the space charge region at the bipolar junction in BPMs and the generation of huge electric fields, which can be utilized for applications like water electrolysis for energy-saving processes.

Chapter 11 outlines the experimental methods used to measure ionic transport properties and transport numbers, including direct current and alternating current techniques. The chapter provides practical insights into theoretical bases and experimental methods like linear sweep voltammetry (LSV), cyclic voltammetry (CV), potentiostatic intermittent titration technique (PITT), and electrochemical impedance spectroscopy (EIS), which are key to characterizing SPEs and IEMs.

Finally, Chapter 12 explores the diverse applications of polymer electrolytes and IEMs in real-world technologies. From secondary batteries and sensitized solar cells to fuel cells and electrochemical water splitting, this chapter provides a comprehensive overview of how the theoretical principles discussed in previous chapters are applied in cutting-edge technologies.

Overall, this part of the book provides an in-depth understanding of ion transport through polymer membranes, emphasizing both theoretical models and their practical applications in energy-related devices.

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