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Mathematical Model of Ion Transport in Electrodialysis Process

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Abstract

Mathematical models of ion transport in electrodialysis process is reviewed and their basics concept is discussed. Three scales of ion transport reviewed are: 1) ion transport in the membrane, where two approaches are used, the irreversible thermodynamics and modeling of the membrane material; 2) ion transport in a three-layer system composed of a membrane with two adjoining diffusion layers; and 3) coupling with hydraulic flow system in an electrodialysis 2D and 3D cell, where the differential equation of convective-diffusion is used. Most of the work carried out in the past implemented NP equations since relatively easily coupled with other equations describing hydrodynamic conditions and ion transport in the surrounding solutions, chemical reactions in the solutions and the membrane, boundary and other conditions. However, it is limited to point ionic transport in homogenous and uniformly - grainy phases of structure. © 2008 CREC UNDIP. All rights reserved.

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Keywords: Mathematical modeling; Ion transport; Membrane stucture; Irreversible thermodynamics; Concentration polarization; Convective-diffusion

1. Introduction

Electrodialysis (ED) is an electrochemical separation process in which charged membranes are applied to separate ionic species from a mixed aqueous solution of varied components under an electrical potential difference It has been widely applied not only in the desalination of natural water, desalination of saline solutions and production of table salt, but also in separation of organic acids and their salts in bio-separation processes. The performance of ionic transport which moves through the electro-membrane depend essentially on two factors: physicochemical properties of the membranes used; hydrodynamic conditions and coupling between the matter transfer in and out the membrane [1].

The mathematical model of ion transport is important in ED process, since it can detail out entire picture of the electrotransport in ED cell. As a result, the mechanism of the ion transport can be described and the performance of the ED can be predicted. The mathematical model the ionic and water transport in ED can be divided into a few types of geometric scales. They are: (1) the membrane; (2) a three-layer system being the membrane with two adjoining diffusion layers; and (3)

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coupling of hydraulic flow in an ED of two-dimensional (2D) and three-dimensional (3D) exhibited in cell. These three scales will be discussed thoroughly in the following section.

2. Transport in Membrane

Both of the transport of solution in hydraulic system which circulates in the space between the membranes and the ion transport in the membranes are noteworthy in the ED process, but the latter predominately determines it performance. The irreversible thermodynamics approach is effective to describe the transport of ions and water through a membrane that treats the membrane as a "black box" and considers the cross effects of all flows through membrane completely. Another kind of model is mathematical modeling taking into account the geometric structure of the membrane, hence, permitting establishment of relation between structure and physico-chemical local parameters with overall physicochemical properties of the membrane.

2.1. Irreversible thermodynamic (IT) approach

In IT theory, the material and energy flow is expressed by the Gibbs equation which has been applied to reversible processes. Because of this assumption, the IT is estimated to realize in the circumstance being close to reversible states. However the theory is considered to be applicable to some extent in the circumstances being apart from reversible state. In the IT, membrane phenomena are treated by combining driving forces with resultant permeation fluxes across a membrane using the phenomenological equation introduced from dissipation function. The IT represents the simplest mathematical tool for linking the flux of species through the membrane with the interfacial concentrations of this species at the left- and right-hand sides, as well as with the external driving forces, the electric current in the case of the ED [2]

The Nerst-Planck (NP) equations, used extensively in this century, provides a simplified approach to mathematical developments, which results in expressions that are easy to use in design of electromembrane, which can be considered as a reduced form of IT equation. The NP equation contains two terms that reflect the contribution of diffusion and electro-migration in the ionic transport. The NP equation may be relatively easily coupled with other equations describing hydrodynamic conditions and ion transport in the surrounding solutions, chemical reactions in the solutions and the membrane, boundary and other conditions [3]. Nernst-Einstein (NE) relation can be applied simultaneously. NE relates the molar conductivity of each ion with its diffusion coefficient, which only one coefficient (normally the diffusion coefficient) per ionic species is necessary, while the diffusion coefficient is expressed by ion mobility [4]. If the convective transport is appended, The NP extended will be formed which includes the velocity of solution. However there are several restrictions which reduce the applications of this equation and, in particular, do not allow this equation to act the role of theoretic basis for the ion [5] .

In the same framework of IT, Kedem - Katchalsky's (KK) equation was developed where the formal thermodynamic treatment of membrane permeability regards the membrane as a geometric transition region between two homogeneous compartments. It was assumed that differences are the driving forces responsible for the corresponding flows through membrane. A set of phenomenological equations was derived to determine the rate all flows. The phenomenological equations were based on practical, straight, and cross coefficient. A series relation was developed for the coupling coefficient which allows a ready transition from one system of coefficients to another [6].

The Maxwell-Stefan (MS) equation in the framework of IT is implemented for multi component diffusion requires one diffusity or friction coefficient for each pair of components in the mixture as transport coefficients. The friction terms are proportional to the local amount (or mole fraction) of the other component which are proportional to the difference in velocity among species. The driving force of MS tends to move down the gradient of its potential. The potential can be divided into separate terms for activity gradients, electrical gradients and other gradients [7].

KK and MS equations do not have restrictions like as NP and are convenient for membrane characterization. Nevertheless, they are quite complicated because of a sufficiently high number of transport coefficients depending on the concentration used.

2.2. Structure Kinetic Models

In this approach the membrane structure is taken into account. It is known that there are many facts directly or indirectly proving that ion-exchange materials, including so-called homogeneous membranes and gel ion-exchangers, are spatially non-uniform. The nonuniformity of ion-exchange membranes has great influence on many physical and chemical properties of ion-exchange systems and their operational characteristics.

Three main classes of mathematical models may be distinguished, depending on the scale of inhomogenieties taken into account when ion and molecule transport in the membrane is being simulated. Classical theories consider a membrane as one homogeneous phase: a solution of matrix polymer chains, fixed and mobile ions and water. Quantitative treatments are based on the equations of irreversible thermodynamics. The classical gel model is the simplest model that assumes the membrane in homogenity structure. The equilibrium electroneutrality relation between number ions in solution and in membrane can be described by Donnan equation which is depended on exchange capacity and mean activitiy coefficients of solution [8] A transport model, where the membrane phase being considered as one species, based on a modified NP equation, taking the tortuosity of the membrane structure into account, was proposed by Higa and Kira [9]. It was shown that the apparent ionic mobility depends not only on the valence of the ion and the membrane potential, but also on the tortuosity. The self-diffusion coefficient in the membrane phase depends on the size of the solvated ions and follows the sequence of mobility observed in aqueous solution. Wesselingh et al. [10] implemented the MS to count the transport coefficient of ion inside a homogenous membrane from free solution diffusity using tortuosity correction. The tortuosity related to void fraction using Marshall's equation. This homogenus membrane approach is quite general. However, the phenomenological coefficients dependent on concentration are very difficult to predict a priori.

The second class of models deals with a thin membrane structure on the submicroscopic scale. Selvey and Reiss [11] proposed model which membrane is treated being a quasi-homogeneous medium with non uniform fixed charge distribution. Species in transport is considered: with the help of continuum flux equations where the electroneutrality is not assumed, so as to include nonlinear effects due to space charge in the quasi-homogeneous medium. The NP and Poisson equations are solved using perturbation theory, and the case of small fluctuations in fixed charge density is considered in order to obtain analytic solutions to the perturbation equations. Hsu and. Gierke [12] proposed model class treats the membrane being a cluster-channel network. Ion transport and current selectivity are best described by percolation and absolute reaction rate theories, respectively. This submicroscopic approach allows the explanation of phenomena of ionic membrane permselectivity. However, since is not taking into account heterophase structure, the model may lead to inaccuracies.

The third class of models studies membrane inhomogeneity on the microphase scale. A membrane is considered as a system of two or several phases, and conductivity properties are found as a function of corresponding phase properties. Zabolotsky and Nikenko [13] proposed a micro-heteogenous model presenting the membrane as a system consisted at least of two phases, as a "gel" phase being an uniformly grainy phases of fixed and mobile ions with the polymer matrix included, and an electroneutral solution phase filling the "intergel" spaces. Inter-gel spaces are inner parts of pores, channels and cavities. The gel phase is considered to be quasi-homogeneous. It is supposed that the NP equations are valid for each phase and for the membrane as a whole, the effective conductance coefficient for the membrane being a function of the respective quantities for each phase. Tugas et al. [14] proposed a three-phase membrane model that incorporates co-ion leakage, comprising hydrophobic polymer, active ion exchange zone and interstitial sorbed zone. The apparent coefficient is accounted using Nernst-Einstein relation. By applying this microscopic membrane approach, the detail coefficient transport in heterogenous phase can be depicted.

All the kinetic structure models proposed are implemented in the small range of low electrolyte concentration. The advantage of this approach is the detail coefficient transport inside the structure membrane can be observed. However, this approach generates quite complicated task of modeling and measurement local structure coefficients to validate the model.

3. Three Layer Model

The three layer model taking into account boundary diffusion layers adjoining the membrane which useful for describing the role of the concentration polarization in the membrane transport. A variation in the interfacial concentrations obtained leads to a variation in the flux or in the effective transport number which is the charge transported by ion. This type of model permits to consider coupling of the membrane transport with different effects of the concentration polarization: limiting current density, water dissociation, homogenous chemical reaction and a space charge macroscopic region [15].

Tanaka [5] developed model which considers the limiting current density effect. The membrane assumed is homogenous. By applying the limiting current density and extended NP equations, solution velocity in the boundary layer, thickness of the boundary layer, concentration distribution in the boundary layer, ionic flux in the boundary layer, electrical current density in the boundary layer and potential gradient in the boundary layer can be determined.

Zabolotsky et al. [16] proposed mathematical model which consider the deviation from the local electroneutrality in space charge region near the depleted solution/membrane interface. The competitive electro-transport of two counter-ions through an ion exchange membrane is described by the NP and Poisson equations. It is shown that the space charge region grows with the voltage applied.

Nikonenko et al. [17] proposed model taking into account coupled homogenous chemical reactions in the external diffusion boundary layers and internal pore solution. A mechanism of competitive transport of anion single electron and anion double electron of weak electrolytes through anion-exchange membranes is described on the basis of the NP and Donnan equations. The model supposes local electroneutrality as well as chemical and thermodynamic equilibrium. It is exhibited that the pH of the depleting solution decreases and that of the concentrating solution increases during ED process.

Tanaka [18] proposed a model considering water dissociation phenomena in ED process. Water dissociation reactions have been analyzed by NP and pH equations. This phenomena base on the equilibrium reached between H2O, H+ ions and OH− ions consist of a forward reaction and a reverse reaction. The forward reaction rate increases along with the increase of electrical potential difference in the water dissociation layer. By applying this model proposed, the forward reaction rate constant of the water dissociation reaction, thickness of the water dissociation layer; and concentration distribution of H+ and OH− ions and electrical potential gradient in the water dissociation layer is exerted.

This approach is still works on homogenous membrane assumption. The complicated task of model will obtained, if the heterogenous structure of membrane is coupled.

4. Coupling hydraulic in electrodialysis using 2D and 3D convective-diffusion model

In this model the transport by convection and diffusion in two and three dimensions is considered in the solution circulated between the membranes in dilute DC and concentration compartments CC. The convective-diffusion model permits to calculate current-voltage curves for an ED cell pair, the distribution of the concentrations and potential in DC and CC, and the longitudinal distribution of the current density and the distribution of velocity and pressure in all compartments.

Shaposhnik et al. [19] proposed 2D model where the solution flow condition assumed is plug flow and laminar. Kinetic in membrane structure is neglected. Velocity profiles obtained, in accordance with the solution of Navier-Stokes equations, have the form of Poiseuille distribution. The analytical solution obtained allows one to calculate concentration fields before, and after the overlapping of diffusion boundary layers

Tanaka [20] proposed 2D model which was demonstrated to consider the nonuniformity solution velocity and the current density due to the pressure distribution in ED stack. The KK equation is implemented for accounting the ion transport through homogenous membrane. Using the Fanning equation, static head difference are expressed by the function of friction head. Friction factor relates to the Reynolds number. The changes of the static head, the velocity head and the friction head in an entrance duct and an exit duct are given using the Bernoulli theorem. By implementing this model the solution friction factor, distribution coefficient of solution velocity and current density may be obtained.

Heranz et al. [21] proposed 2D model where the flow condition is pulsated. The model presents the effect of pulsation frequency, pulsation amplitude and fluid velocity on the wall shear stress of the inner cylinder of an annular duct composed by an anionic membrane in laminar flow. The mass transfer across the anionic membrane is calculated numerically for different pulsation parameters (frequency, amplitude and fluid velocity), solving the mass balance equation. As a consequence of the pulsation, the shape and thickness of the concentration boundary layer change with time, and vortices are developed through a pulsation period due to the instability of the concentration boundary layer caused by the pulsating flow. The mass transfer enhancement across an ion exchange membrane in pulsating flow may be due to the periodic renewal of the liquid in the wall boundary layer as can be concluded by the formation of the vortices and their dispersion in the bulk of the solution.

Tanaka [22] developed 3D convective-diffusion model which is obtained due to coupling with natural convection phenomena. Mass transport with natural convection in a boundary layer near the surface of a vertical membrane is a three-dimensional process. The ionic flux in a boundary layer is divided into the fluxes of diffusion, migration and convection. The solution velocity in a boundary layer is divided into the velocities of electro-osmosis, concentration-osmosis and natural convection. They are consistent with the equation of continuity. The 3D convective-diffusion model permits to determine velocity convection on three components direction. The convective-diffusion model is the coupling hydrodynamic system with membrane and three layer models. Thereby, the whole system of ED can be represented. The summary of the model discussed are summarized in Table 1.

5. Conclusion

The three main scale: the membrane; a three-layer system being the membrane with two adjoining diffusion layers; and coupling of

TABLE 1. Summary – models applied in ED process.

No	Model	Model class	Geometrical scale	Reference
1	Nernst – Planck (NP)	Irreversible thermodynamic	Membrane	Buck, R.P, 1984
2	Nernst – Enstein (NE)	Irreversible thermodynamic	Membrane	Pourcelly, et al., 1996
3	Nernst – Planck extended	Irreversible thermodynamic	Membrane	Tanaka, 2003
4	Kedem – Katchalsky (KK)	Irreversible thermodynamic	Membrane	Kedem and Katchalsky, 1963
5	Maxwell -Stefan (MS)	Irreversible thermodynamic	Membrane	Wesselingh, et.al., 1995
6	Donnan , membrane gel	Homogenous structure	Membrane	Lakshminarayanaiah, 1969
7	NP, membrane tortuosity	Homogenous structure	Membrane	Higa and Kira, 1994
8	MS , membrane tortuosity, Marshall void fraction	Homogenous structure	Membrane	Wesselingh, et al, 1995
9	NP-Poisson, quasi homogenous phase.	Submicroscopic structure	Membrane	Selvey and Reiss, 1985
10	Percolation and absolute reaction rate theories, cluster channel network.	Submicroscopic structure	Membrane	Hsu and. Gierke, 1983
11	NP, membrane two phases (gel – intergel)	Microscopic structure	Membrane	Zabolotsky and Nikenko, 1993
12	NE, membrane three phases	Microscopic structure	Membrane	Tugas, et al. 1993
13	Extended NP	Limiting current density at double layers	Three layer	Tanaka, 2003
14	NP- Poisson	Space charge deviation at double layers	Three layer	Zabolotsky et al, 2002
15	NP- Donnan, chemical equilibrium	Homogenous chemical reaction at double layer	Three layer	Nikonenko et al, 2003
16	NP- pH equation	Water dissociation at double layers	Three layer	Tanaka, 2002
17	Convective – diffusion, Navier - Stokes	2D uniform flow	Hydraulic coupled	Shaposhnik et al, 1997
18	Convective – diffusion, Fanning and Bernoulli theorem	2D nonuniform flow	Hydraulic coupled	Tanaka, 2004
19	Convective – diffusion, pulsation factor	2D pulsed flow	Hydraulic coupled	Heranz et al, 1999
20	Convective – diffusion, continuity	3D- natural convection coupled	Hydraulic coupled	Tanaka, 2004

hydraulic flow in an ED of two-dimensional (2D) and three-dimensional (3D) exhibited in cell have been reviewed and their basic concepts was discussed. It is found that most of the previous work implemented NP equations since relatively easily coupled with other equations describing hydrodynamic conditions and ion transport in the surrounding solutions, chemical reactions in the solutions and the membrane, boundary and other conditions. However, it is limited to point ionic transport in homogenous and uniformly - grainy phases of structure. From the review above, developing model which can depict a whole ED process considering the membrane structure, three layer and hydrodynamic condition in the larger range of concentration and flow velocity is still needed.

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