Model analysis on electrodialysis for inorganic acid recovery and its experimental validation

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ABSTRACT

Theoretically, conventional electrodialysis (ED) technology should have played important roles in the reclamation of acid-containing discharge. However, at present, it is seriously restricted by some unresolved problems and badly in need of deep understanding. Accordingly, the model analyses on an ED process for acid recovery are performed for a possible prediction and effective optimization in this study. Above all, the negative contributions from the electro-migration and concentration diffusion to the acid-recovery process were firstly isolated by means of a series of well-designed experiments. Results indicated that the potential gradient and concentration difference did play significant roles in the undesired transport of protons. Especially, the acid leakage is practically proportional to the corresponding driving forces, which contributes to accurately predict the corresponding negative contributions on the basis of a deep understanding on the characteristics of the acid-recovery system and ED stack configuration. Furthermore, a concentration evolution model was established, which paved a road for the subsequent calculation of process energy consumption with aid of some classical mathematical expressions and parameter measurements. Practical ED experiments showed that the simulation results were in good agreement with the experimental data, which verified the validity of the proposed model.

1. Introduction

Various inorganic acids such as hydrochloric acid, sulfuric acid and nitric acid are indispensable in many industrial processes, such as acid pickling, electroplating, steel making and even water treatment itself. With the growth of population and development of economy, the inorganic acid consumption must keep an increase in future. For example, the Information Handling Services consulting company has estimated a moderate increase in the consumption of sulfuric acid of about 2% per year for the forecast year of 2014–2019 [1]. Inevitably, excess quantities of low-grade waste acids are generated, for example, being enriched with heavy metals, relatively low concentration (e.g. below 5%) and huge effluent volume. According to a roughly estimation, more than 25 million tons per year waste acid is produced in China [2]. Whether from the view of environmental protection or economy in resources, the treatment of acid-containing discharge has become a matter of great urgency.

Although the neutralization-precipitation-discharge technique is still employed for the treatment of waste acid up till now, many techniques have been put forward based on the idea of waste acid reclamation [3,4]. Therein, ion-exchange-membrane-based techniques,

such as diffusion dialysis (DD) [5–10], electro-electrodialysis (EED) [11], electrodialysis (ED) [12–14] and other upgrading schemes [15–16], are the typical representatives. In DD process for acid recovery, the ion transport across anion exchange membranes (AEMs) is driven by the concentration gradient with observation of the Donnan criteria of co-ion rejection and preservation of electrical neutrality. As a spontaneous process, DD has been widely applied due to its significant superiority, such as low energy consumption, low cost and easy operation. Every coin has two sides. DD is also significantly restricted by the concentration of waste acid which significantly influences its processing capability, processing efficiency and the maximum recovered concentration. Just the same as DD, EED for acid recovery makes only use of AEMs. EED can recover acid with a higher concentration and even simultaneously achieve metals by means of the electrochemical reactions at the electrodes. However, the requirements of many working electrodes (e.g. a pair of electrodes for every unit) and generation of hydrogen lead to higher capital and operating costs. Obviously, there is still a long way to go before putting EED into large-scale applications. In ED process, an alternate installation of the AEMs and cation exchange membranes (CEMs) allows the relevant ions able to cross the AEM to be stopped by the CEM and vice versa. Thus, ED

technology should have been employed in the reclamation of the acid-containing aqueous solutions for the water purification and acid concentration. In particular, in view of the continuous improvements in membrane preparation, such as the acid-block AEM and the mono-valent selective CEM, the application prospect of ED for the reclamation of waste acid is worth anticipating.

As well known to all, a mathematical model can be regarded as a powerful tool to assist the decision makers to evaluate and examine many alternatives with minimal efforts, for example, the optimized options of an ED process and design of an ED plant. According to extensive literature, it can be found that different modeling approaches for ED process have been proposed mainly for the salt systems on the basis of Nernst–Planck equation [17–20], Stefan–Maxwell theory [21,22], irreversible thermodynamics formalism [23–26], mass balance of separation system [27–29] and some semi-empirical models which involved some experimentally determined parameters related to membranes and membrane stack [30]. However, as far as we know, the special transport mechanisms of proton which are fundamentally different from those of other ions, such as Grothuss mechanism and Vehicle mechanism, often results in the notorious proton leakage across AEM [31]. Therefore, there must exist some distinctive characteristics in the modeling of ED process for the reclamation of acid-containing discharge. Unfortunately, the literature concerning this topic is poor besides [32].

In this work, the negative contributions from the electro-migration and concentration diffusion to the inorganic acid transport in an ED process were firstly isolated by means of well-designed experiments. Based on these, the ED process of strong acid system can be mathematically described. Hopefully, the predictions on the ED process for the acid recovery, including its concentration evolution and energy consumption under the relevant operating conditions can be carried out accurately after achieving some important model parameters.

2. Experimental

2.1. Membranes

Three kinds of typical commercial AEMs were selected in this work, including Qianqiu heterogeneous AEM (Zhejiang Qianqiu Environmental Protection & Water Treatment Co. Ltd., China), ACM AEM (ASTOM Corporation, Japan), and Fumasep FAB AEM (FuMA-Tech GumbH, Germany). In addition, Fumasep FKB CEM (FuMA-Tech GumbH, Germany) was used together in the ED experiments for acid recovery.

2.2. Limiting current density

In view of the limited reference value of some lab-scale investigations on the influences of hydrodynamic conditions on an ED process, the effects of some operating conditions on acid-recovery performances, including applied current density, concentration difference between the diluted and concentrated compartment, membrane selection, acid species and concentration, were explored under the same flow state in this work. Thus, the limiting current density can be described by an empirical equation which was only related to the dilute tank concentration (C_d):

$$j_{lim} = A \cdot C_d^\alpha \tag{1}$$

Herein, the A and α coefficients can be determined by measuring a series of limiting current values corresponding to different dilute tank concentrations.

2.3. Membrane electrical resistances

Membrane electrical resistances were obtained by the impedance measurements using the four-electrode technique. The investigated

membrane sample embracing an effective area of 0.785 cm^2 was clamped in an electrochemical cell which was composed of two compartments of equal volume (about 50 mL). Two surfaced platinized titanium plates were used as working electrode (WE) and counter electrode (CE), respectively. Another two saturated calomel electrodes (SCE) which were employed as reference electrodes (RE) were inserted into a Luggin capillary and placed closely to the membrane surface as much as possible. Impedance spectra were recorded by CHI660E Electrochemical Workstation (Shanghai Chenhua, China) in the frequency of 1 Hz–100 kHz. The amplitude was 0.01 V. A frequency region over which the impedance had an almost constant value can be observed in a Bode plot. The electrical resistance can be read from the corresponding Nyquist plot. Thus, membrane electrical resistances (R) can be determined according to the following equation.

$$R = (|Z|_{mem} - |Z|_{blank}) \times Area_{mem} \tag{2}$$

Here, $|Z|_{mem}$ and $|Z|_{blank}$ denote the impedance value with and without membrane, respectively. $Area_{mem}$ is effective membrane area.

Electrical resistance of IEM is closely related to the equilibrated electrolyte solution, including its composition and concentration. In this study, the average value of the series of membrane electrical resistances which were measured in the different acid concentrations (for example, 0.1 M–1 M HCl) was regarded as membrane electrical resistance for the subsequent model simulation.

2.4. Ion transport number

2.4.1. Ion transport number in electrolyte solution

The ion transport number is generally assumed to be independent of electrolyte solution because it is only a weak function of solution concentration and temperature. Accordingly, the ion transport number (t_i) can be expressed in terms of the limiting molar electrical conductivity [33]

$$t_i = \frac{\lambda_{i,m}^\infty}{\Lambda_m^\infty} \tag{3}$$

$$\Lambda_m^\infty = \nu_- \lambda_{m-}^\infty + \nu_+ \lambda_{m+}^\infty \tag{4}$$

Herein, Λ_m^∞ is the limiting molar conductivity, ν_- and ν_+ are anion stoichiometric number and cation stoichiometric number, respectively.

2.4.2. Ion transport number in IEM

Many studies have indicated that unsatisfactory ED performance for acid recovery mainly lies in proton leakage of AEM. Thus, the ion transport numbers in AEM were paid more attention in this study. The AEM was clamped between two half-cells into which acid solutions with different concentrations ($C_1 = 0.5$ M and $C_2 = 0.1$ M) were fed, respectively. Then, the membrane potential (E_{mem}) can be measured at ambient temperature by a couple calomel reference electrodes which were inserted into a pair of Luggin capillaries. During the experiments, the solution was circulated in the corresponding compartment by a peristaltic pump (LEAD15-44, Baoding Longer Precision Pump Co. Ltd.) to reduce the influence of boundary layer. At last, the transport number can be estimated according to the following equation.

$$E_{mem} = \frac{RT}{zF}(2\bar{t}_a - 1)\ln\frac{C_1}{C_2} \tag{5}$$

Herein, $\bar{t}_a$ is the anion transport number in the membrane, R is the universal gas constant, F is the Faraday constant, T is the test temperature, and z is electrovalence of counter-ion.

2.5. Ion diffusion coefficient

The ion diffusion coefficient (D_i) can be obtained according to the Stokes–Einstein equation: