

Advances in electrodeionization technology for ionic separation – A review

Khoiruddin, A.N. Hakim and I.G. Wenten^{*1}

Department of Chemical Engineering, ITB, Jl. Ganesha 10, Bandung 40132, Indonesia

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Abstract. Electrodeionization (EDI), which combines electrodialysis (ED) and conventional ion-exchange (IX), is a mature process which has been applied since more than twenty years on commercial use for the production of ultrapure water (UPW). Eliminating chemical regeneration is the main reason for its commercial success. The increase in acceptance of EDI technology has led to an installation of very large plant as the commercial state of the art that produces 1,500 m³/h of water for high pressure steam boiler. More recently, EDI system has found a number of new interesting applications in wastewater treatment, biotechnology industry, and other potential field. Along with further growth and wider applications, the development of stack construction and configuration are also become a concern. In this paper, the principle of EDI process is described and its recent developments, commercial scale, and various applications are pointed out.

Keywords: electrodeionization; electrodialysis; ion exchange resin; ultra pure water; ion exchange membrane

1. Introduction

The concept of modified electrodialysis (ED) process, well known as electrodeionization (EDI), has been extensively recognized since the mid-1950s. After the first commercial unit introduction in 1987 (Ganzi *et al.* 1987), EDI has continued to be an attractive deionization process with significant advantageous than conventional ion exchange deionization (IX-system) in production of ultrapure water (UPW) from technological and economical standpoint (Wood *et al.* 2010, Fedorenko 2004). The main reason for its commercial success is that EDI eliminates regeneration process and its associated hazardous chemical. As a chemical free operation or environment-friendly technology, this process is increasingly becoming the dominant choice for UPW production (Wood 2008, Parker 2011, Liang 2003). EDI is mainly applied for water and wastewater treatment, but it has also shown potentials to be applied in a number of different applications. Some previous comprehensive review papers with focus on production of UPW and some applications have been found (Wood *et al.* 2010, DiMascio *et al.* 1998, Fu and Wang 2008, Wang *et al.* 2011, Wang 2005). Therefore, this review will complement previous reviews on EDI technology. In general, this paper covers brief principle and recent development in EDI technology.

^{*}Corresponding author, Ph.D., E-mail: igw@che.itb.ac.id

Furthermore, large scale applications, membrane manufacture, and process economics of EDI system are pointed out.

2. Process overview

The typical schematic of EDI process is shown in Fig. 1. An EDI module (stack) has the similar components as those used in ED wherein cation exchange membrane (CM) and anion exchange membrane (AM) are employed as active separators. Both membranes are packed in alternating arrangement between electrodes (anode and cathode) while spacer is inserted in between to form an individual compartment. A stack generally comprises of several pairs of diluate and concentrate compartments and a pair of electrode compartment. In EDI, the diluate compartment sometimes also the concentrate and electrode compartments are filled with electrically active media (usually cation-exchange resin or CR and anion-exchange resin or AR) thus differs from ED. When an electrolyte solution is transferred through those compartments and an electrical potential from the electrodes is established, the cations and anions migrate towards the cathode and anode, respectively. The cations pass through the CM and excluded by AM. In the otherwise, the anions pass through AM and excluded by CM. The ion concentration of electrolyte solution is depleted in diluate compartment and concentrated in concentrate compartment. Mechanism of ion removal in EDI contains two main principles as explained by Ganzi *et al.* (1992). The first step is a process of which the ions in the feed water are bound to the ion exchange resins, wherein the cations are exchanged with H^+ ions and anions are exchanged with OH^- ions. The second step is a process of which the ions bound to the resins are transported by the electrical force through the ion exchange membrane surfaces into the concentrate compartment. These two main principles only occur at the early stage. After the process reaches its steady state, ion exchange resins mainly function as ionic bridge that will increase the overall conductivity of the diluate compartment.

Performances of EDI for ionic separation have been compared to ED process e.g. elimination of nitrate (Salem *et al.* 1995), water demineralization (Dejean *et al.* 1998), removal of hardness ions (Park *et al.* 2007), demineralization of brackish water (Larchet *et al.* 2008), and NaOH recovery (Keramati *et al.* 2010). EDI has showed better performance than ED especially for

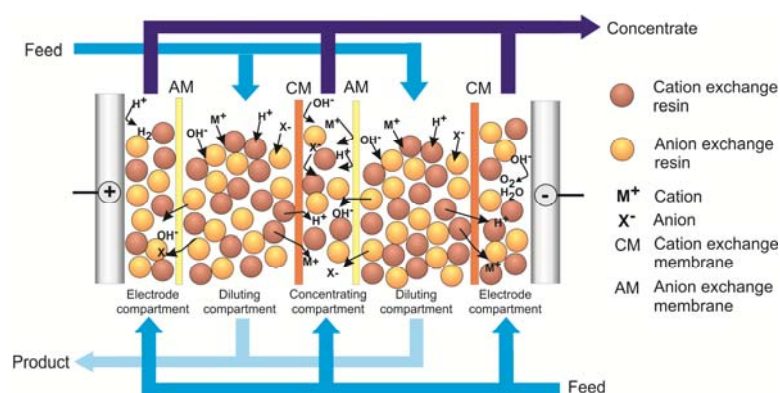
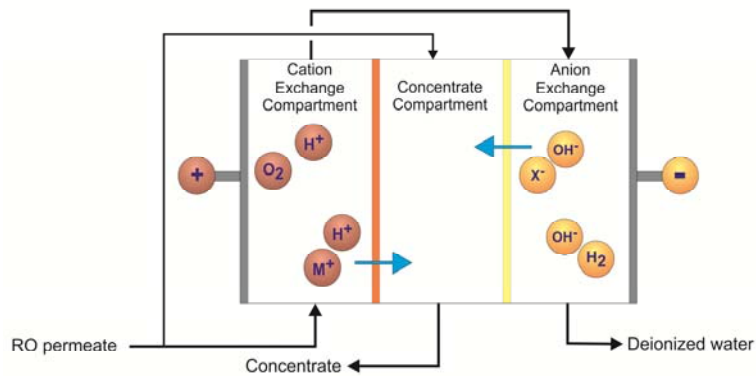


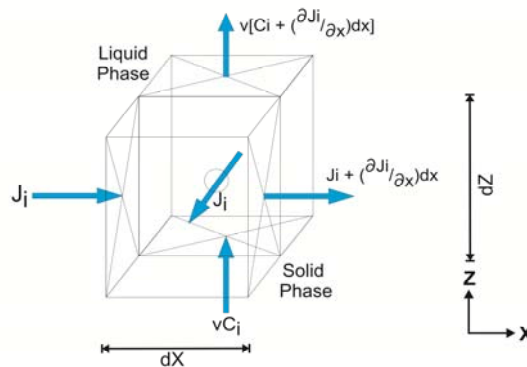
Fig. 1 Schematic diagram of EDI process

dilute solution due to higher electrical conductivity provided by ion exchanges filling. However, the commercial applications of EDI are still focusing on high purity water production since EDI can remove weakly ionized components efficiently through extensive water dissociation.

Verbeek and co-workers (1998) have proposed the concept expressing mass transport in EDI using separated ion-exchange resin beds as can be seen in Fig. 2(a). Accordingly, water-splitting reaction needed for regeneration of the resin beds occurs at electrode interface which are in direct contact with the resins. Therefore, it is possible to describe the mass transfer process without water dissociation inside the beds and to present ions fluxes in liquid and solid (resin) phase in differential balance element (Fig. 2(b)). In the liquid phase, the change of ion concentration is expressed on z-axis direction since convection dominates the mass transfer and axial dispersion can be neglected because of high liquid velocity (Eq. (1)). While in the solid phase, counter-ion flux is expressed on x-axis direction due to external electrical field and diffusion can be neglected (Eq. (2)). Ionic transfer from liquid to resin is totally controlled by diffusion in the liquid film formed on resin surface, based on Nernst-Planck Equation (Eq. (3)). And for neutral ion (k), the flux is expressed by conventional equation (Eq. (4)).



(a) EDI with separated ion-exchange resin beds



(b) Material balance for liquid and solid phase

Fig. 2 Mass transport model (Verbeek *et al.* 1998)

Where C_i and \bar{C} are concentration of counter-ion in liquid and resin phase, a_s is specific surface of resins, ε is resin porosity, t is time, J and \bar{J} are molar flux of individual ion in liquid and resin phase, respectively, D is diffusion coefficient, u is mobility of counter-ion, ϕ electric potential in the liquid film, and ζ is Space coordinate in the liquid film. In the case of UPW production, the following ions are considered to be important: H^+ , Na^+ , K^+ , NH_4^+ , Ca^{2+} , Mg^{2+} , OH^- , Cl^- , NO_3^- , SO_4^{2-} , HCO_3^- , CO_3^{2-} , $SiO(OH)^-$, and in addition dissolved neutral CO_2 , and $Si(OH)_4$. Some of these components are coupled by chemical reactions (Eqs. (5)-(10)).

Liquid Phase

$$\frac{\partial C_i^b}{\partial t} = -v \cdot \frac{\partial C_i^b}{\partial z} - a_s \cdot \frac{1-\varepsilon}{\varepsilon} \cdot J_i \quad (1)$$

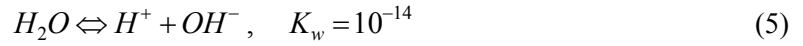
Solid Phase

$$\frac{\partial \bar{C}_i}{\partial t} = a_s \cdot J_i - \frac{\bar{J}_{electr,i}}{\partial x} \quad (2)$$

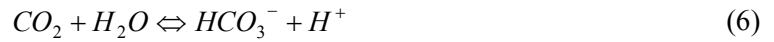
$$J_{i/j} = -D_{i/j} \cdot \frac{\partial C_{i/j}}{\partial \zeta} - z_{i/j} \cdot C_{i/j} \cdot u_{i/j} \cdot \frac{\partial \phi}{\partial \zeta} \quad (3)$$

$$J_k = -D_k \cdot \frac{\partial C_k}{\partial \zeta} \quad (4)$$

Water dissociation



Carbonate system



$$\frac{C_{H^+} \cdot C_{HCO_3^-}}{C_{CO_2}} = K_{C1} = 10^{-6.43} \quad (7)$$



$$\frac{C_{H^+} \cdot C_{CO_3^{2-}}}{C_{HCO_3^-}} = K_{C2} = 10^{-10.33} \quad (9)$$

Silica system



Because co-ions (j) are not absorbed onto resins and they are not involved in the chemical reaction, then their total fluxes J_j become zero (Eq. (11)). On liquid film surface, there is no net current (Eq. (12)). And at every position inside the liquid phase, electroneutrality are applied (Eq. (13)).

$$J_{j,nr} = 0 \quad (11)$$

$$\sum_{i=1}^m (z_i \cdot J_i) + \sum_{j=1}^n (z_j \cdot J_j) = 0 \quad (12)$$

$$\sum_{i=1}^m (z_i \cdot C_i) + \sum_{j=1}^n (z_j \cdot C_j) = 0 \quad (13)$$

The main driving force for ionic transport in the solid phase is external electric field (φ), therefore diffusion can be neglected since resulting fluxes are much smaller than fluxes caused by migration. Then the counter-ion flux in the solid phase can be expressed by Eq. (14). Finally, the total electric current I remains constant, thus the gradient of potential field for the whole depends on solid phase concentration (Eq. (15)). Here, d is compartment thickness and b is width of the cell. From numerical simulation results of this model, shows that compartment thickness is one of the most important design parameters.

$$J_{electr,i} = -z_i \cdot \bar{u}_i \cdot \bar{C}_i \cdot \frac{\partial \varphi}{\partial x} \quad (14)$$

$$\frac{\partial \varphi}{\partial x} = - \frac{I_{tot}}{\frac{F \cdot (1 - \varepsilon) \cdot b}{d} \int_{z=0}^I \int_{x=0}^d \left(\sum_{i=1}^n (z_i^2 \cdot \bar{u}_i \cdot \bar{C}_i) \right) dx \cdot dz} \quad (15)$$

The electrical current, I , required to remove a number of ions is given by Eq. (16). Where z is the valence, F is the Faraday's constant (1 Faraday = 96,500 As/equiv.), Q is the flow rate, ΔC is the concentration difference between the feed and the diluate (mol/l), and η is the overall current efficiency. Meanwhile, an energy required (E , Watt.second) to transport the amount of ions can be calculated by using Eq. (19) which combining Eq. (16)-(18).

$$I = \frac{z F Q \Delta C}{\eta} \quad (16)$$

$$E = V \cdot I \cdot t \quad (17)$$

$$V = I \cdot R \quad (18)$$

$$E = I^2 \cdot R \cdot t \cdot \frac{z F Q \Delta C}{\eta} \quad (19)$$

In EDI process, there are three main regions appeared in the current-voltage relations as reported by Song *et al.* (2007) which is shown in Fig. 3. In Region I, EDI is operated in low current density, wherein current increased linearly with applied voltage. This region is known as transport region of salt ions which is characterized by a linear increase in current density with applied voltage up to limiting current density (I_{lim}). The limiting current density is reached when ion concentration at the membrane surface in the diluate compartment goes towards zero

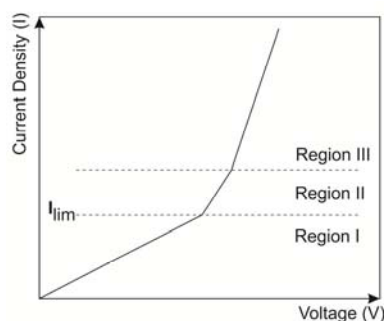


Fig. 3 Current-Voltage relationship

(Strathmann 2010). Meanwhile, a high current density is applied in Region III which the current density steeply increased. Region III is also defined as water diffusion limitation region that is the current limitation as the result of a decrease in the H^+ and OH^- ion concentration by diffusion limitation of water molecules into the transition region. Also a curvature region or Region II which is known as water dissociation region, existed between those two linear regions. In Region II, a drastic increase occurred as the result of H^+ and OH^- migration that are produced within the bipolar interface due to depleted ionic solution. However, the water diffusion limitation region is not observed in the study. Since water molecules are continuously supplied through convective flow to bipolar surface, thus those region was disappeared in EDI system. Accordingly, EDI is usually operated under overlimiting current regime (Region III) to attain more intensive mass transfer for treating dilute solution (Larchet *et al.* 2008). Electroconvection effect contributes to this enhancement of mass transfer.

Water dissociation is found in electro-membrane processes due to concentration polarization phenomena that takes place at bipolar interfaces of ion-exchange resins and ion-exchange membranes which in contact each other and form resin-resin and resin-membrane interfaces (DiMascio and Ganzi 1999, Meng *et al.* 2004). When the ion concentration inside depletion layer is sufficiently small, the water dissociation occurs at the bipolar interface and carried a significant part of electrical current. Some investigations of water splitting have been conducted and found that water splitting on membranes (AM or CM) could increase ions removal (Fei *et al.* 2012, Lu *et al.* 2010, Danielsson *et al.* 2009). It rapidly regenerates resins and accelerates the removal of weakly ionized component such as silica and boron. Besides, the regenerated CR (H-form of resin) can bringing more salts of interstitial solution into the resin phase that produces high conductivity channel for cation migration (Lu *et al.* 2010). Nevertheless, one should be noted that, extensive water splitting due to concentration polarization will reduce the current efficiency and thus will increase energy consumption.

EDI has many attractive features, such as a unique “electro-regeneration” for regenerating the resins. Therefore, the resins are never fully exhausted and chemical regenerant is not needed. The cost for chemical regeneration process that usually used in conventional IX-system including labor and chemical are replaced by small amount of electricity (Willis 2008). EDI can be operated in continuous process while duplexing such as in conventional process is not necessary. EDI is able to produce pure water with high resistivity (Larchet *et al.* 2008) and high salt rejection to more than 99% which cannot be achieved by a conventional ED (Wang *et al.* 2000). Moreover, no obvious

Table 1 Effect of operating parameters on ions removal

Ref.	Solution	Feed	Flow (L/h)	Current density (A/m ²)	Removal (%)
Dejean <i>et al.</i> 1998	NaCl	30 mg/L	60	200	≈ 35
		150 mg/L	60	200	≈ 10
		300 mg/L	60	200	≈ 5
		3 mg/L	60	5.0	≈ 25
		3 mg/L	60	10.0	≈ 30
		3 mg/L	60	16	≈ 38
Song <i>et al.</i> 2005	RO-permeat	10 μ S/cm	0.6	20	≈ 99
		20 μ S/cm	0.6	20	≈ 99
		30 μ S/cm	0.6	20	≈ 98.5
		2.3 μ S/cm	0.6	2	≈ 65
		2.3 μ S/cm	0.6	5	≈ 80
		2.3 μ S/cm	0.6	10	≈ 90
		2.3 μ S/cm	0.6	20	≈ 98
Xing <i>et al.</i> 2009	Cr (VI)	40 mg/L	1.2	50	≈ 99.8
		50 mg/L	1.0	50	≈ 99.6
		50 mg/L	1.2	50	≈ 99
		10 mg/L	2.0	196	92
		25 mg/L	2.0	196	94

limiting current point was observed in EDI performance (Liu *et al.* 2008a, Wang *et al.* 2003). With those advantages, EDI has shown superior performance in water desalination and gain attention for large scale applications.

The effects of operating parameters on EDI performance are shown in Table 1. The main technological parameters determining the performance of EDI technique are the current strength and voltage, flow velocity in the diluate and concentrate compartment, temperature and ions concentration (inside both feed and product water), pressure, and the degree of conversion (Fedorenko 2003, Li *et al.* 2009, Wang and Wang 2001, Salem 2000). The amount of ions transported through ion exchange membrane is directly proportional to current density (Ervan and Wenten 2002, Kurup *et al.* 2009) and temperature (Song *et al.* 2005). Ions migration increases at higher current density and higher temperature, since the mobility of ions is increased thus resulting in higher removal. But the removal rate is not further increased when the current density is higher than optimal value (Song *et al.* 2005). As aforementioned in the process overview, too higher current applied leads to reducing current efficiency wherein the significant part of current is applied to dissociate water and thus resulting in high operating cost due to high energy consumption. Therefore, EDI should be operated under optimal current density. Optimal current density was estimated at the minimized area of electroregeneration regime (Bouhidel and Lakehal 2006, Lee *et al.* 2007). Removal efficiency was found to be inversely proportional to the feed flow (Song *et al.* 2005, 2007) and feed conductivity (Song *et al.* 2005). When the feed flow increases, it appears to cause a decreasing contact time of solution with resin beads. It reduces the migration of

ions from solutions to ion-exchange beads. On the other hand, as feed conductivity increases, higher ion concentration is needed to be removed and it results in lower diluate resistivity. Meanwhile, there is improvement in the current density when the feed conductivity increased.

3. Increased of EDI design

3.1 Reducing the overall module resistance

Attempts to reduce the overall module resistance have focused on (Liang and Wang 2001): development of strongly acidic and strongly basic ion exchange membranes that can catalyze the water splitting reaction, improvement of weak ion removal, and reduction of the resistance of concentrating stream. Several methods to reducing the resistance of concentrate compartment are recirculation of the concentrate stream in a feed and bleed configuration, injection of a salt solution into the concentrate stream, and addition of ion exchange resin to the concentrate compartment. It is preferable to lower the module resistance by using ion exchange resin in the concentrate and electrode cells as well as the dilute cells, to make the resistance independent to conductivity of concentrate stream (Gifford and Atnoor 2000, Wood and Gifford 2002, Wood *et al.* 2004) because the ion exchange beads are more conductive than the water to be treated (Decker 2010). This type of configuration is called all-filled EDI. Besides, studies on cell configuration found that the added resin in concentrate streams actually picks up silica or CO₂ from its stream and quickly sweeps them away from the membranes, reducing the chances for back-diffusion, and minimizing concentration polarization (Jha and Gifford 2000).

3.2 Ion exchange filler and stack configuration

There are several type of resin configurations inside the cells, those are: mixed bed, clustered bed, layered bed, and separated bed (Liang and Wang 2001). In the mixed bed EDI, the water dissociation takes place mainly in resin-resin and resin-membrane bipolar boundaries. The presence of reverse junction between ion-exchange resins of different polarity interrupts the migration of ions through the beads thus limits the thickness of compartment (Grabowski *et al.* 2008). EDI with mixed beds resin also shows a poor removal of weak acids and bases (Grabowski *et al.* 2008). The separated bed type showed a better performance for high-purity water production (Thate *et al.* 1999). A better removal of weakly ionized components can be obtained in EDI with bipolar membrane (BM) wherein CR and AR are placed in separate beds with a BM placed in between (Strathmann 2010). The function of BM is to generate proton and hydroxyl ions which are transported to CR and AR containing compartment respectively for carrying out continuous regeneration of resins. Both mixed bed and separated bed are applicable and generally used in commercial scale (Strathmann 2010). Eventhough the separated beds with BM shows better removal of weakly ionized component compared to mixed bed EDI, it is still facing another problem of product contamination due to cations diffusion from concentrate into diluate compartments (Grabowski *et al.* 2006). The diffusion of cations is attributed to incomplete permselectivity of the AM. Grabowski and co-workes (Grabowski *et al.* 2006, 2008) have investigated EDI with BM which contains a so-called “protection compartment or PC” between diluate and concentrate compartment (Fig. 4). A PC is placed in between diluate and concentrate compartment and filled with AR. The PC is also rinsed with low conductivity water, such as a part of diluate water. The cations penetrating from concentrate compartment is rinsed in PC before

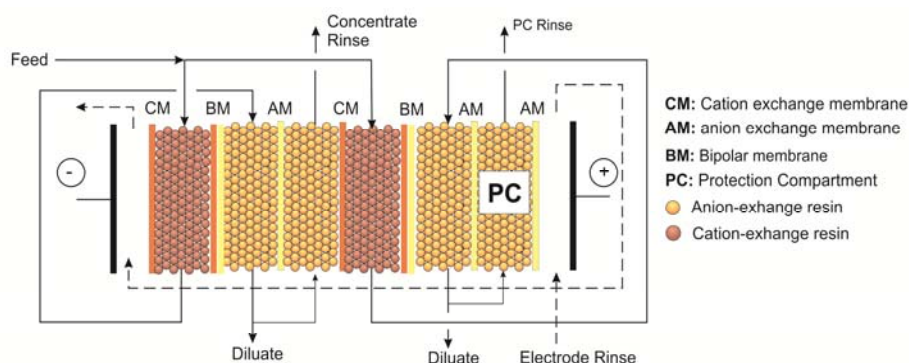


Fig. 4 Various resin configurations (Grabowski *et al.* 2008)

reaching the diluate compartment. Thus the product water conductivity can be strongly reduced using this PC because the co-ion penetrating into the diluate could be eliminated. In spite of the excellent performance of EDI-BM with PC, the use of PC increases the number of compartments in the stack and results in higher capital and operating cost.

The clustered bed and layered bed provide a continuous migration path of ions, prevent the formation of reverse junction, and improve deionization performance of weakly deionized electrolytes (Grabowski *et al.* 2008, Feng *et al.* 2010, Yeon and Moon 2003). However, EDI with clustered or layered beds have main drawbacks due to different water dissociation rate and conductance of the CR and AR which then leads to different current densities through the beads and differences in both regeneration (Grabowski *et al.* 2008). Besides, to establish such clustered and layered bed configuration, a special spacer design is required to obtain those resin arrangement inside the compartment thus resulting in high cost for stack construction.

Several research and development in EDI stacks are focusing on resin beads alternatives such as: ion-exchange textiles (Yeon *et al.* 2004a, Elleuch *et al.* 2006), ion-exchange fibers (Yoshida *et al.* 2002, Liu *et al.* 2011), and porous ion-exchanger (Inoue *et al.* 2007); immobilization of resins inside the cell (Yeon *et al.* 2004b, Ho *et al.* 2010); spacer geometry (Grebenyuk *et al.* 2007, DiMascio *et al.* 2003); and ion exchange resin arrangement inside the cells (DiMascio *et al.* 2003, Franzreb 2006, Ganzi *et al.* 2001). Those developments were conducted to obtain several goals which include: reduction of pressure drop, improvement of hydraulic condition, increase the conductivity, and avoid the problem of resins channeling or agglomeration.

3.3 Removal of weakly ionized component

Generally, in EDI process, compounds that are predominantly dissociated and in ionic form are more easily transported under the influence of an electric field than are those such as boron, silica and dissolved CO₂ that may not be dissociated, and may exist in a predominantly non-ionized form. The removal of those compounds becomes important in the production of UPW and every trace constituent present in the feed water must be removed. Results of some studies showed that boron and silica removal can be improved by: arrange the ratio of AR to CR (Sato 2010), adjust the pH value (Liang *et al.* 2004, Osawa and Kato 2002), applying opposite current direction between diluate feed water and concentrate feed water (Shinnei and Kakuda 2001), increasing electric

current (Wen *et al.* 2005), decreasing total dissolve solids of feed water, and apply low current efficiency (Sato and Takayuki 2004). The pH of water solution strongly affects the removal of silicon and boron due to ionic formation of both components provided by hydroxyl ions. The ratio of AR to CR may alter the pH due to unbalanced composition of cations and anions inside the compartments which induce more hydroxyl ions. Likewise, the increasing of electric current leads to the increasing of water dissociation rate thus the hydroxyl ions are more generated. As consequence, the EDI is operated under low current efficiency. In alternative approach, applying counter-current flow between diluate and concentrate stream will improve the removal efficiency. The counter-current flow avoids silicon and boron back diffusion from concentrate to diluate compartment. Back diffusion mechanism of CO₂ from concentrating to diluting compartment and imperfect permselectivity of ion exchange membrane are also responsible for degradation of EDI performance. Studies on guard channel showed that, the back diffusion processes virtually eliminated by using the guard channel, and flowing the water, purified or feed water in the concentrating compartment (Mir 2001). CR and AR the guard channel act as transfer layer for ions to the middle of concentrating compartment. However, the use of such channel may result in stack complexity and high construction cost.

4. Electrodeionization applications

4.1 Production of UPW

As reviewed previously, EDI process has now been in commercial use for over twenty years and has gained widespread acceptance in the production UPW for industrial use. The UPW variety applications including pharmaceutical manufacturing, steam generation or power plant (Li *et al.* 1998, Wood 2008), microelectronics or semiconductor manufacturing (Fulde 2004, Gebicke *et al.* 2003, Menzel and Beusshausen 2006), and academic and clinical laboratories (Riviello and Siriraks 2011). The industry with the most stringent UPW quality is likely semiconductor wafer fabrication, which desires water with ionic, particulate, and organic contaminants concentration below detection level. Several related industry with similar requirements are manufacturing microelectronic devices, solar panels, or flat-panel displays. Standard design to obtain UPW, uses combination of RO and EDI. With this design, the system can produce water which has specific ions concentration near or below detection limits (Sanz *et al.* 2006). Prato and Gallagher (2000) reported the using of EDI for UPW production in power plant boiler makeup water and microelectronics fabrication rinse water. Although it was used in two different fields of application, report shows that EDI meets and exceeds the specifications of both the microelectronics and power industries. In those plants, EDI removed about 97-99 % silica and 97% boron with 16-18 MΩ-cm of product resistivity. Meanwhile, the TOC concentrations in product water were about 90 ppb (52% removal) and 40 ppb (37% removal) for power plant and microelectronic plant, respectively. Besides, EDI also able to remove viable bacteria and endotoxins in experiment (Harada *et al.* 2011) that suitable in medical procedures, especially haemodialysis and related therapies. In addition, incorporating hot water sanitization to the system is also possible for controlling bacteria and biofilm growth (Wood *et al.* 2000).

4.2 Wastewater treatment

In recent years, there are also growing interests in EDI for wastewater treatment. Removal of

Table 2 Performance of EDI in wastewater treatment

Ref.	Solution	Feed con. (mg/L)	Removal rate (%)	Enrichment factor	Diluate
Feng <i>et al.</i> 2008	Cu ²⁺	–	99.5	5.0 – 14.0	0.23 mg/L
Lu <i>et al.</i> 2011	Nickel	50	99.8	31	> 1 MΩ·cm
Taghdirian <i>et al.</i> 2010	Cobalt	66.6	99	–	0.31 mg/L
Gayathri and Kumar 2010	Cr (VI)	312	98 – 100	8	–
Souilah <i>et al.</i> 2004	Zn	34.4	–	85	–
Basta <i>et al.</i> 1998	Pb ²⁺	10	> 95	–	< 1 mg/L
Jones <i>et al.</i> 2006	HF	250	–	80	–
Li <i>et al.</i> 2010	Sr ²⁺	–	–	–	58~114 mg/L
Liu <i>et al.</i> 2008b	Sr ²⁺	–	> 95	–	–
Lounis <i>et al.</i> 2007	Uranium	23.6	–	–	< 1.5 mg/L
	Molybdenum	40	> 98	–	< 0.8 mg/L

heavy metal ions from industrial wastes is considered as extremely important problem. A wide range of wastewaters containing heavy metals are produced in manufacturing processes, such as electroplating wastewater. Some studies were intended to evaluate the effectiveness of the continuous EDI process as a pollution prevention technology by treating and recovering or reusing wastewater. The performance of EDI for wastewater treatment are listed in Table 2. In 2010, EDI was applied for NaOH recovery from waste stream of Merox tower (Keramati *et al.* 2010). The study showed that EDI was successful for NaOH recovery especially at low voltages. However, to apply EDI process for this application, it is necessary to convert Na₂S salt existing in the waste stream to harmless salts by Serox process.

An integrated membrane system combining RO and EDI was used for simultaneous sugar concentration and salts removal from a synthetic dilute sugar solution as a model of sugar-containing wastewater (Widiasa and Wenten 2007). Two different operation modes, i.e., RO-EDI and EDI-RO, were assessed. The experimental results showed that the observed sugar rejection of RO membrane was more than 99.9% and there was no sugar loss in the EDI stack. This indicated that the hybrid process allows almost total sugar recovery. In addition, significant reduction of salts content from the concentrated sugar solution was obtained.

Scaling in membrane surfaces during the removal of multivalent ions may encounter in EDI process. The scaling usually formed in concentrate compartment particularly in AM surface. Anions such as hydroxyl ion are highly concentrated in membrane solution interface both in diluate and concentrate compartment. However, the latter is the surface with the highest concentrated anions. As the cautions migrate toward anode, the cations are precipitated and scaling is formed on AM surface in the presence of high concentration of hydroxyl ions. Applying a periodic polarity reversal can mitigate the scaling formation on membrane surface during deionization process. Deposited ions on the surface of membranes are pulling back when the polarity of electrode is reversed. Therefore, this method can avoid membrane scalling (Lee *et al.* 2012).

Table 3 EDI applications in biotechnology and biopharmaceutical

Ref.	Application	Scale	Performance
Widiasa <i>et al.</i> 2004	Citric acid concentration	Pilot scale	Recovery: up to 50%, concentrating up to 60,000 ppm.
Yu <i>et al.</i> 2006	Separation and esterification of cation salt carboxylates	Lab scale	Esterification conversion up to 40%, productivity up to 40 mg.L ⁻¹ .h ⁻¹ .
Arora <i>et al.</i> 2007	Production and separation of gluconic and lactic acid	Lab scale	GFOR produced continuously for 7 days with production rates up to 1000 mg.L ⁻¹ .h ⁻¹ at > 99% product recovery
Eliseeva <i>et al.</i> 2009	Recovery of basic amino acids	Lab scale	Recovery: ornithine tartrate: 98%; lysine tartrate: 90%; ornithine bitartrate: 82%; lysine bitartrate: 79% and histidine bitartrate: 63%
Li <i>et al.</i> 2011	Production of methyl methoxyacetate	Lab scale	Concentration of methoxyacetate up to 1.8 mmol.dm ⁻³
Du <i>et al.</i> 2012	Separation of Butyric acid	Lab scale	Butyric acid in product was 92%

4.3 Biotechnology and biopharmaceutical

The use of EDI technique in biotechnology and biopharmaceutical are also challenging. Since dilute solution has relatively high electrical resistance, using electrically active media as the bridge over current is a strategy to decrease the resistance and the energy consumption (Huang *et al.* 2007). By adopting this strategy, low concentration solution can be treated by using EDI process. The applications of EDI including separation and purification of biotechnology product and organic acid productions are summarized in Table 3. In spite of their potentials, most of those applications are still in laboratory scale thus more developments are needed by EDI towards commercialization in this field. Industrialization of ED and related process in organic acids production are facing challenges that have been discussed in literature (Huang *et al.* 2007). The challenges include: (i) decreasing ion exchange membrane cost especially for the BM; (ii) eliminating or reducing membrane fouling; and (iii) improving ion exchange membrane selectivity. Among them, fouling is the most significant problem which limits the industrialization. Several method can be taken to reduce membrane fouling including: (1) periodically reversing the polarity of electrodes; (2) lowering current density; (3) hydraulic improvement inside compartments; (4) chemicals addition to suppress the formation of precipitates and the propagation of microbes; (5) extracting products before saturation; (6) employing membrane with tailored properties; and (7) membrane cleaning during shut down.

4.4 Other applications

Besides of those aforementioned fields of application, some other applications are including pollution control and water softening. EDI has successfully removed low concentration of pollutant in contaminated water such as nitrate and ammonium (Meyer *et al.* 2000, 2005a, b, Bi *et al.* 2011, Spiegel *et al.* 1999). EDI with reversal polarity process or EDIR, shown the feasibility as softening process with high removal efficiency and recovery (Park *et al.* 2007, Lee *et al.* 2012,

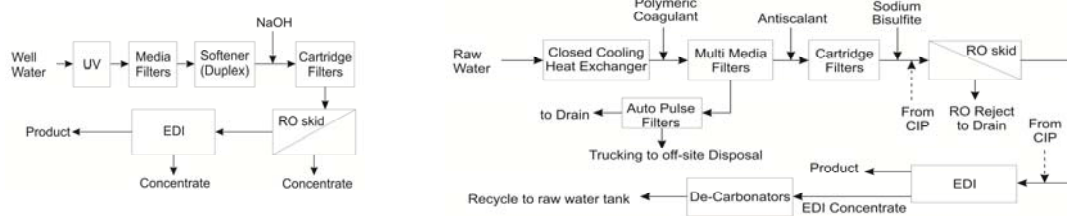
2013). In addition, EDIR showed lower resistance and energy consumption than EDR. EDIR system was successfully demonstrated without scale formation in reasonable concentration range during water softening process (Lee *et al.* 2012).

5. Large scale EDI system

Table 4 shows several EDI plants in commercial scale. In 2001, as reported by Wood *et al.* (2003), the Nelson Dewey Generation Station located on the Mississippi River in Cassville Wisconsin decided to replace the existing conventional ion exchange beds which previously used as RO polisher with EDI system. The RO/EDI system was applied for boiler make up water. Fig. 5(a) shows the schematic diagram of RO/EDI system. Feed water was taken from well water. Ultraviolet device, media filter, softener, and cartridge filter were installed as the pretreatment prior to RO. A so-called “all-resin-filled” EDI module was used in the system which allowed operation without concentrate salt injection or concentrate recirculation. In addition, to reduce CO₂ load on EDI system, caustic injection was installed prior to RO. The system was able to produce demineralized water with conductivity of 0.06 $\mu\text{S}/\text{cm}$ and 50 ppb silica. Ho and Wood (2006) reported design, construction, and operation of the largest commercial RO-EDI plant which located at Con Edison’s Steam system, New York. RO/EDI system was used to provide demineralized water as make up for steam generators. The steam generating capacity was expanded from 2.7 to 5.7 million pounds/hours which accomplished by installation of a 1,500 m³/h demineralization facility. The water system was designed to consist of two parallel trains that comprised of pre-filtration, chemical addition, RO, and EDI. A schematic diagram of the system is shown in Fig. 5(b). The plant commissioning began in early 2005 and commercial operation began in April. After an initial stabilization period, product water quality has been consistently less than 0.1 $\mu\text{S}/\text{cm}$, < 15 ppb silica, and < 3 ppb sodium. Other typical processes in EDI system include ultrafiltration membrane (UF), RO, and EDI. The UF membrane provides water that is required

Table 4 Commercial scale EDI

Ref.	Location	Year of operation	Capacity (m ³ /h)
Beattie 2001	Amgen Building, Thousand Oaks, CA	1997	5.7 – 7.3
www.gewater.com	Fiat Rivalta Plant, Italy	1998	30
Wood <i>et al.</i> 2003	The Nelson Dewey Generating Station, Mississippi River, Cassville Wisconsin	2001	11.3
www.water.siemens.com	Rijnmond Energy Center, the Netherlands	2004	170
Ho and Wood 2006	Con Edison’s steam system, New York City	2005	1500
Garcia and Lehtinen 2010	Storuman, Sweden	2008	55
www.dowwaterandprocess.com	Shanxi Sanwei Cogen Plant, China	–	520
	Shandong Zhucheng Cogen Plant, China	–	225
	Qingdao Hengyuan Cogen Plant, China	–	180
www.ges.co.il	Termocalendaria, Colombia	2008	120
www.enersave-group.com	Wafer Fab Ultra Pure Water System in, Singapore	2009	340



(a) The Nelson Dewey Generating Station

(b) Con Edison's steam system, New York City

Fig. 5 Schematic diagram of commercial scale EDI system (Wood *et al.* 2003, Ho and Wood 2006)

for RO and replaces the conventional pretreatment. This kind of process design was utilized in Shanxi Sanwei, Shandong Zhucheng, and Qingdao Hengyuan Cogen plants (Table 4).

6. Ion exchange membrane manufacture and modules

In EDI process and general electro-membrane processes, ion-exchange membranes are utilized as key separators. Traditionally, ion-exchange membranes are classified into anion-exchange membrane and cation-exchange membrane which contain positively and negatively charged groups, respectively. The ion-exchange membranes are expected to possess: high permselectivity, low electrical resistance, good mechanical stability, and high chemical stability (Kariduraganavar *et al.* 2006). Commercial ion-exchange membranes can be divided into two major categories: homogeneous and heterogeneous ion-exchange membranes. A comprehensive review on ion-exchange membrane preparation can be found in literature (Kumar *et al.* 2013, Nagarale *et al.* 2006). To date, commercial EDI modules are available in two major configurations: plate-and-frame or spiral wound (Dey 2005, Dey and Tate 2005a, b, Rychen *et al.* 1997). The plate-and-frame modules are similar to a plate heat exchanger, with multiple fluid compartments layered between a set of endplates and electrodes which are held in compression. Meanwhile, the spiral wound modules are similar to RO modules. It comprises a plurality of membrane and spacer leaves that are rolled to form a cylindrical element. While the spiral wound EDI modules have been around for more than a decade, the plate-and-frame configuration still dominates the installation of EDI system (Wood 2008). In the plate-and-frame module, all the diluate compartments are identical to each other (as well as for concentrate compartments) and both hydraulic flows and current density are evenly distributed among the cells. In the otherwise, an equal distribution of current density could not be obtained in spiral wound membrane since the outer leaves have more membrane area than the inner one. The recent development of EDI module is the use of a round shape plate in "stacked disk" configuration inside a fiber-reinforced plastic (FRP) vessel as a mechanical support (Liang *et al.* 2003). The FRP vessel is used to simplify system plumbing using RO-like interconnectors to manifold together EDI module in parallel. The modules then can be placed in a frame like those usually used for RO pressure vessel.

7. Process economics

In economical point of view, EDI is an effective technology alternative to IX as polishing unit

Table 5 Comparison of RO/IX and RO/EDI system cost (Matzan *et al.* 2001)

System	Parameter	Cost (\$)
Capital cost		
RO-IX	Main system: (i) single pass RO system, two trains; (ii) granular activated carbon system, two parallel, three-column trains; (iii) mixed bed deionization system, three trains	1,015,221
	Ancillary facilities: (i) bulk chemical supply for regeneration; (ii) neutralization tank with pH monitoring and system control; (iii) regeneration skid	119,990
	Area required: 324 m ²	279,200
	Annual operating cost	-
	Acid (\$ 2,102); caustic (\$ 13,140); manpower (\$ 4,088); waste water (\$ 6,137); resin (\$ 5,820).	31,267
	Capital cost	
RO-EDI	System: (i) Single pass RO system, two trains; (ii) granular activated carbon system, two parallel, three-column trains; (iii) EDI system, two trains	925,608
	Area required: 268 m ²	268
	Annual operating cost	-
	Actual without brine: Electrical consumption (\$ 8,405); manpower (\$ 2,044); waste water (\$ 0); stack replacement (\$ 0);	10,449

following RO. The RO-IX process is now broadly used as the final water treatment step to produce high purity water due to its high removal efficiency, simplicity, and easy operation (Noh *et al.* 1996, Spiegler 1966). As an alternative to ion exchange process, EDI can be combined with RO process as pretreatment to assure better performance stability. EDI feed water quality requirement can be divided into two categories. The first relates to the performance of the module. Increasing the TDS or CO₂ in the feed water would not cause permanent damage to the module, but it may impact the product quality. The second category includes items that could damage the module, such as heavy foulants like organics and hardness. These requirements can be easily achieved by pretreatment of single or double pass RO.

Matzan *et al.* (2001) provided an economic comparison of EDI and IX for UPW production. The comparison of capital and annual cost are summarized in Table 5. In this study, comparative assessment of the efficiency of ultrapure water production by RO-EDI and RO-IX methods are presented. It was found from this assessment that EDI is less expensive than IX-bed in capital cost and projected annual operating cost based on pilot test. Furthermore, the EDI system required smaller footprint and the main working cost are including electricity, labor for maintenance, and stack replacement. Manpower for EDI maintenance is less than for conventional IX system since it takes few times for data logging and manual adjustment, whereas the regeneration and cleaning of IX system takes several hours for each regeneration. The wastewater in EDI system is generated from concentrate and electrode stream that can be blended with RO concentrate and being recovered for several industrial uses. In contrast, wastewater generated from conventional IX system should be neutralized prior to disposal. Therefore it requires a neutralization system. The

similar economic analysis has been conducted by Fedorenko (2004) for comparing RO/IX and RO/EDI system. Capital and annual costs of IX and EDI systems are compared in different feed TDS (low, medium, and high TDS from RO permeate) and various output capacity. Results of investigation showed that the annual operating costs for all EDI (low to high TDS and product capacity) were lower as compared to those in IX system. EDI system with low and medium capacity exhibited advantages over conventional IX system with respect to capital cost. More recent study on EDI performance and economic evaluation was conducted by Wenten *et al.* (2013). The economic analysis of RO/EDI system was conducted in comparison with the existing conventional ion exchange beds during bench scale test. Likewise, they concluded that EDI showed good water quality and had surpassed existing demin water specification. Besides, the specific water cost was lower than existing demin water system. However, in this study, stack replacement was estimated as one of the main operating cost which in contrast to that reported by Matzan *et al.* (2001) (see Table 5). This is because the stack lifetime was assumed to be 3 years in order to accommodate the worst condition.

The integration process of RO-EDI has become a technology for producing UPW with high quality water, lower cost, and environmental friendly. RO delivers high quality water that meet EDI requirement while EDI provides excellent polishing step with remarkable silica and boron removal. Recently, Li *et al.* (2013) have proposed a novel concept of desalination system that combined RO and reverse electrodialysis (RED). The RED unit function is to generate energy from salinity gradient while treating waste brine from RO concentrate. This concept could be integrated to RO-EDI pure water plant as an alternative for RO concentrate management and energy saving.

8. Conclusions

EDI technology, which combines ED and conventional IX-bed processes, is one relatively new process which has only recently begun to be used in the production of UPW on a large scale. The main reason for its commercial success is that EDI has the advantage of no chemical-regeneration or chemical-free operation. In addition, EDI method is more effective than the conventional IX-bed from both technological and economical point of view. Nowadays, development of EDI process is growing further and other applications beyond production of UPW have been studied. EDI technique appears to have many other potential uses such as wastewater treatment, separation and production of biotechnology product, and some other potentials applications. By employing ion exchange media inside the cells, EDI is expected to be an effective deionization process for the treatment of solution with high electrical resistance in comparison with ED. However, application in biotechnology requires more development to overcome several problems toward commercialization especially fouling mitigation on membrane surface. Along with wider applications, various modifications of the original EDI stack design have been developed in recent years to improve process efficiency including electrical efficiency, packing resin inside the stack, and removal of weakly ionized substances.

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