Development of bipolar membrane-based processes

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Abstract

Recently, a bipolar membrane-based process has become one of the most attractive fields in the world from both academic and industrial points of view. The intention of this paper is to give a brief overview and technical advantages as well as some experimental results by using bipolar membranes in the areas of environmental engineering, chemical production, bioengineering, energy sources, etc.

Keywords: Bipolar membrane; Water dissociation; Environmental engineering; Clean production; Energy sources

1. Introduction

A bipolar membrane (BM) is a kind of composition membrane that at least consists of a layered ion-exchange structure composed of a cation selective membrane (with negative fixed charges) and an anion selective membrane (with positive fixed charges). Similarly, the discovery of semiconductor N–P junctions has brought about the invention of many new semiconductor instruments, and this composition of anionic and cationic exchange layer brings about many novelties [1–8] such as separation of mono- and divalent ions, anti-deposition, anti-fouling, water dissociation, etc. Particularly, water dissociation based on a bipolar membrane technology, which is regarded as one of the most promising fields,

has acted as a new growth point in electrodialysis industries due to its superiority to conventional water electrolysis. The energy consumption for electrolysis process is 198.5 kJ/mol, while for electrodialytic water splitting it is only 79.9kJ/mol [9,10]. This low energy consumption not only means a saving in power but also, because less heat is generated, the necessity for cooling is diminished. Additionally, bipolar membrane water splitting does not generate any gases such as H_2, O_2 and Cl_2, and thus there is no corrosion to both cathode and anode. Due to these advantages, a bipolar membrane and its related technology have found many applications in industries and in daily life, such as chemical production and separation, environmental conservation etc. The involvement of a bipolar

membrane in these fields can significantly change the features of the conventional processes and eliminate the potential contamination to the environment. So it has been considered to be simple, energy-saving, and environmentally benign technology. This paper will give a brief introduction to the potential applications of bipolar membrane technology for its applications in environmental engineering, chemical production, energy sources, bioengineering, etc.

2. Chemical production and separation

Bipolar membranes are able to electrically separate water into hydrogen and hydroxyl ions. When used in conjunction with a conventional cation and/or anion membrane as well as in conjunction with conventional unit operation such as extraction or adsorption in a stack, they provide a low-energy, simple process for chemical manufacture and separation as described below.

2.1. Production of acid and base from the corresponding salts [11–13]

This is well known technology that originated from bipolar membrane dissociation. In this process there are two main kinds of cell arrangements: one is a two-compartment unit and the other is a three-compartment one as shown in Figs. 1(a) and (b). The two-compartment unit is simple in structure, but the base produced from the cathode has a tendency to be transported to the acid compartment through the anion membrane and neutralize the acid produced from water dissociation and thus decrease the current efficiency. This disadvantage is overcome by a three-compartment unit. Moreover, in a three-compartment configuration, there are no direct contacts of cation layer with acid and anion layer with base, and thus the duration of a membrane is significantly increased. In fact, concentration of
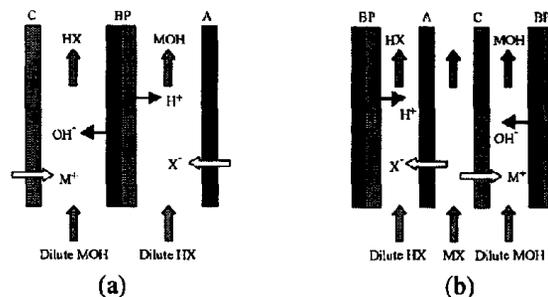

Fig. 1. Fundamental cell arrangement for production of acid and base from the corresponding salts. C, cation membrane; A, anion membrane; BP, bipolar membrane; HX, acid; MX, salt; MOH, base. (a) Two-compartment cell. (b) Three-compartment cell.

the produced acid and base can be attained as high as 6 mol.L^{-1} by using this configuration [13]. In China, this new technology has been used in industry to manufacture silica acid (H_2SiO_3) from Na_2SiO_3. Compared with the conventional ion-exchange method, the energy consumption can decrease from 1 kwh.kg^{-1} products to 0.6 kwh.kg^{-1} products at a current density of 10–12 mA.cm^{-2}.

2.2. Electro-extraction and back-extraction [14]

This is an integrated technology from many disciplines. An example given here is extraction of copper from cupric solutions. As shown in Fig. 2, the feed containing copper is circulated from compartment 1, and the extractant organic phase containing ion-exchange resin is filled in compartment 2. When voltage is applied, cupric ions and other cations are transported through a cation membrane from compartment 1 to compartment 2 where it is selectively extracted under the weak base condition that is controlled by the water splitting rate. The copper-rich organic phase is circulated to compartment 3 at the right where back-extraction takes place and cupric ions are released and transport to compartment 4 under the condition of acidity produced from the water dissociation. And thus, the net result is that
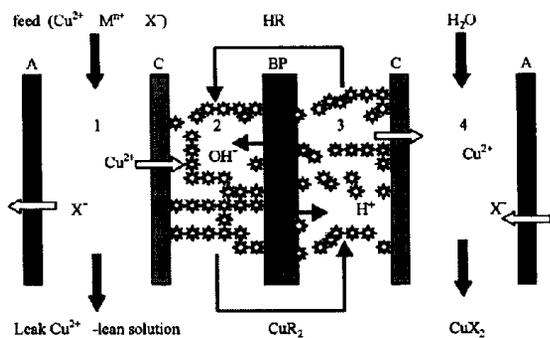
Fig. 2. Concentrating cupic ions by bipolar electro-extraction. HR, extractant; ✿ represents the ion-exchange resin.
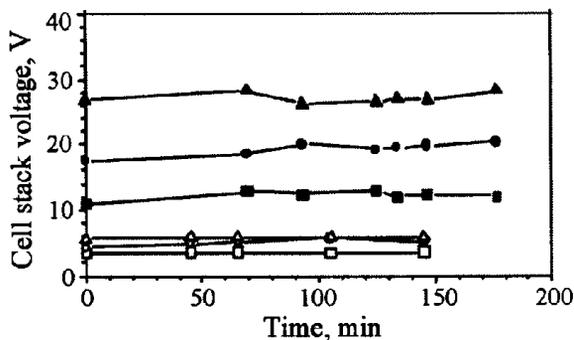

Fig. 3. Cell voltage changes at various current densities: 50 (square), 80 (circle) and 100 (triangle) mA.cm^{-2}, respectively, for electro-extraction. Solid symbols for D001 porous resin and open symbols for 001*7 resin.

if the feed is circulated from compartment 1, the copper-rich aqueous phase can be obtained in compartment 4. No additional extractant is necessary in the process nor is the conventional back-extraction needed. The operation is a combination of ion exchange, extraction and water dissociation. The ion-exchange resin plays a decisive role in the process because it not only acts as a bridge for the exchange between ions and the organic phase but also increases the conductivity of the organic phase and thus decreases the operation voltage. We use two kind of ion resin produced at the Nankai Chemical Plant (China): D001 porous cation resin and 001*7 gel cation resin for recovering copper from its dilute solution [14]. We found that the voltage of the cell stack, whose configuration is shown in Fig. 2, was strongly affected by the resin. As shown in Fig. 3, the cell voltages for resin D001 is much higher than those for resin 001*7 at various current densities; moreover, the former is more dependent on the current densities. The calculated current efficiencies are 0.85–0.90 at 40 mA.cm^{-2}, 0.70–0.84 at 80 mA.cm^{-2} and 0.44–0.65 at 100 mA.cm^{-2} for D001 porous resin, and 0.88–0.95 at 40 mA.cm^{-2}, 0.67–0.78 at 80 mA. cm^{-2} and 0.56–0.62 at 100 mA.cm^{-2} for 001*7 gel resin. Therefore, an average efficiency of

90% can be achieved if the process is operated below 50 mA.cm^{-2} by using gel resin.

2.3. Separation of ions with same charge and same sign

Tsuru et al. [15] reported the separation of ions with different valence using a bipolar membrane. The process is based on the valence difference and the ion repulsion. But if the ions have equal valence, separation seems to be impossible by this mechanism. This kind of separation is expected to occur by an integrated process of a bipolar membrane water splitting with coordination or adsorption as shown in the following examples.

The first example illustrated here is the separation of Co^{2+} and Ni^{2+}. This separation is realized by a bipolar membrane electrolytic cell stack 1 (left in Fig. 4) and a conventional cell stack 2 (right in Fig. 4). The mixture containing Co^{2+} and Ni^{2+} was fed into compartment 2 of the left cell and complex agent (denoted as HR) and added to compartment 3 of the left one. When voltage is applied, both Co^{2+} and Ni^{2+} are transported to compartment 3 in the direction of the current, where they tend to coordinate with a complex agent and form a complex. Since the
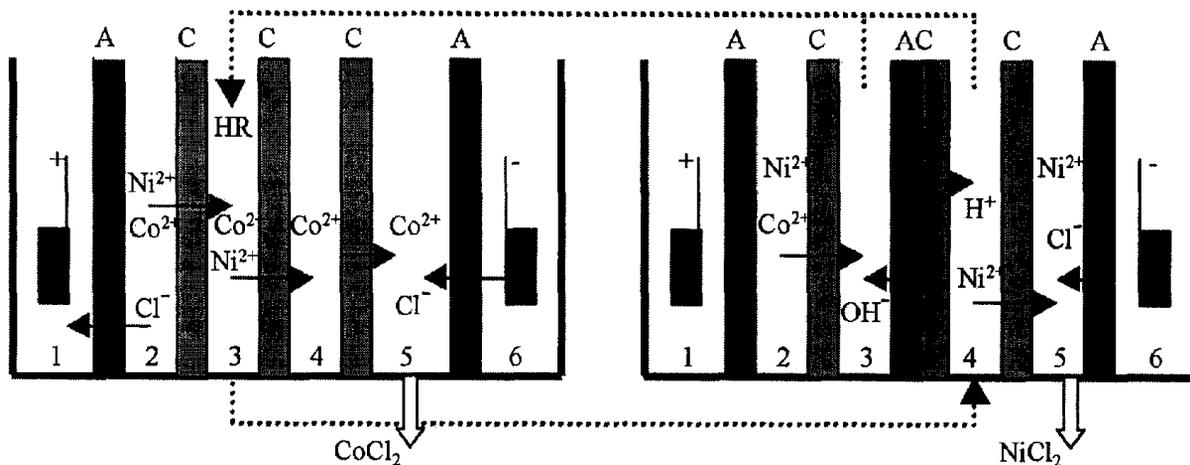
Fig. 4. Schematic diagram for cobalt and nickel ions.

stability for complex NiR_2 is much greater than CoR_2, so Co^{2+} has a weak ability to coordinate and be transported to compartment 4 and finally retained in compartment 5, which contains no complex agent. The solution of complex NiR_2 was circulated into compartment 4 of the right cell where the complex agent is recovered by the protons produced from water dissociation. The recovered agent was fed back to compartment 3 of the left cell and the released Co^{2+} transported to compartment 5 of the right cell. To neutralize the systems, the basic solution in compartment 3 of the right cell was also circulated to compartment 3 of the left cell to neutralize the acid produced from the complex process. Thus the net result for the above process is that Co^{2+} is accumulated in compartment 5 of the left cell and Ni^{2+} in the compartment 5 of the right cell. Mo et al. showed that the concentration ratio of Co:Ni can be attained as high as 20:1 in compartment 5 of the left cell and 1:20 in the corresponding chamber of the right cell if the feed contains $CoCl_2$ and $NiSO_4$ with an equal molar concentration of $0.15\,mol.L^{-1}$ and the current efficiencies for both electrodialyser are above 70% [2,16].

Another example is the separation of ions in ocean chemical industries. As we know,

separation or enriching of potassium and iodine from seawater or other mixtures is very difficult but of great importance. The available method is the adsorption by using zeolite adsorbents. However, this method has brought a series of problems such as low separation efficiency and difficulty in desorption, etc. A combination of adsorption and bipolar membrane-water splitting provides an attractive measure for treating with such problems. Taking the separation of potassium from the mixed metal ions as an example, the cell for this purpose is shown in Fig. 5(a). The mixture is circulated through the left compartment where it is pre-packaged with zeolite. As zeolite has a stronger tendency to adsorb potassium, so the potassium is retained in compartment 1. The adsorbed potassium will be desorbed by the protons produced from water dissociation when voltage is applied and then migrated in the direction of the electrical field to compartment 2. Thus, in this compartment we can get potassium with a relatively high concentration. The separation of iodine with other anions is almost the same as the above process except that the positions of the anion- and cation-exchange membrane were reversed as shown in Fig. 5(b). Interestingly, if we combine Fig.5(a)
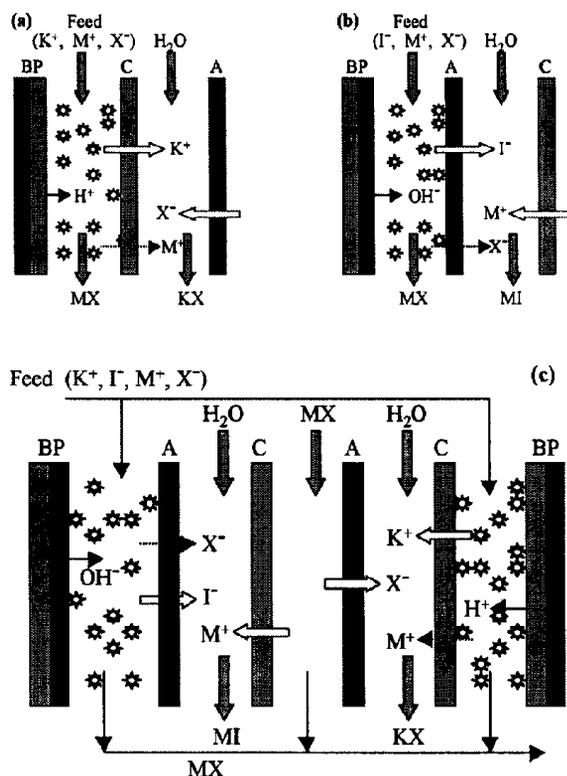
Fig. 5. Separation of iodine or potassium based on a simultaneous bipolar membrane and adsorption process. (a) Separation of potassium; (b) separation of iodine; (c) simultaneous separation of iodine and potassium. ❁ represents zeolite, M^+, cations; X^-, anions.

and 5(b) as shown in Fig. 5(c), a simultaneous separation of both iodine and potassium can be achieved [17]. Our preliminary results showed that the separation factors for K^+/Na^+ are about 8.2 and for I^-/Cl^- about 10.2. Permselectivity can be enhanced further by choosing the appropriate adsorbents. Obviously, a bipolar membrane permits a continuous separation process for this aim.

3. Environmental applications

3.1. Recovery/purification of acid and bases from the spent liquors [18–20]

The application of a bipolar membrane based process to purify acid and base stream is based

on the recognition that the bipolar membrane can act as a highly selective cation or anion membrane in a conventional electrodialysis-type operation. Acid and base streams contaminated with varying levels of cationic and anionic impurities occur from many industrial operations such as sulfuric acid from lead acid batteries, caustic soda from a $NaOH/NaNO_3$ mixture in Ni/Cd battery manufacture, HCl and NaOH from ion-exchange regeneration streams, sulfuric acid from aluminum anodizing baths, nitric acid from uranium processing operations, HNO_3 and NH_4NO_3 systems in rare earth industries, mineral acids from mining/metal recovery operations, etc. Though there are several available technologies such as neutralization/diffusion dialysis using an anion-exchange membrane filtration to treat these streams, direct recovery using the conventional method offers a significant, more cost-effective route for recovering these materials because these streams often contain substantial amounts of free acid or base. When a bipolar membrane is used in this manner, it provides an effective means for purifying acids and bases and can archive product purification and concentrations that are not achievable via conventional electrodialysis, diffusion dialysis or ion retardation techniques.

The cell configuration for acid recovery is shown in Fig. 6(a). The assembly is similar to a conventional elactrodialysis except that the bipolar membranes replaced the conventional cation membranes. As shown in Fig. 6(a), the feed compartment bounded by the anion side of the bipolar membrane and the anion membrane is fed with the impure acid stream contaminated with cations of metals such as Na, Fe, Cr, Cd, Ai, Ti, etc. Water or dilute acid is fed to the product chamber bounded by the cation side of the bipolar membrane and the anion membrane. When a direct current is passed between the electrodes, hydrogen ions from the bipolar membrane are introduced into the product compartment. Simultaneously, the electric current causes the transfer of anions across the
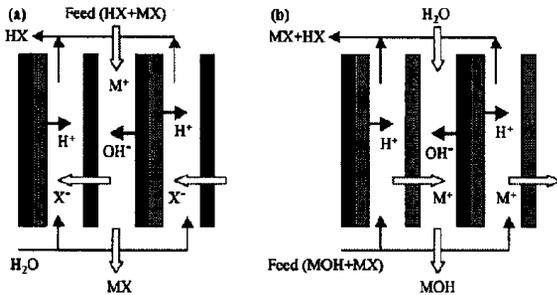
Fig. 6. Schematic drrawing for acid (a) and base (b) recovery and purification u nit.

anion membrane to the product compartment and form acid. The concentration of acid in the feed compartment is reduced as a result of the anion and net hydrogen transport to the product compartment. The resulting product acid stream is recovered from the product compartment while the treated feed stream (depleted in its acid content) is removed from the feed compartment.

The cell configuration for base purification is similar to the above with the cation membrane replacing the anions membranes as shown in Fig. 6(b), the purification process work in a manner analogous to the acid purification cell. The impure is introduced into the compartment bounded by the cation side of the bipolar membrane and the cation membrane. The feed is typically contaminated with anions such as Cl^-, NO_3^-, SO_4^{2-}, etc. Cations from the impure base stream were transported across the cation membrane to the product compartment (bounded by the cation membrane and the anion side of the bipolar membrane). Here they combine with the hydroxyl ions formed at the bipolar membrane, resulting in a purified base product.

Graillon et. al. used this technology to treat the concentrated nitrate effluents from an ammonium nitrate solution [19]. This treatment involved two steps in case of leakage of ammonium through the membranes. The first is the ammonium stripping after neutralization of the NH_4NO_3 by base (NaOH or KOH) and then the water splitting to regenerate NaOH (or KOH) and

at the same time produce the HNO_3. This process allows the regeneration of nitric acid and base which can be recycled in the industrial process and is an example of a clean technology with zero effluent production (zero nitrate rejection).

3.2. Control of fluorine leakage from uranium fluoride production

In the production of uranium fluoride (UF_6), it is inevitable to discard the waste gases or liquid containing 50–500 ppm fluoride and organic. The common treatment is the neutralization with KOH and then the precipitation with $Ca(OH)_2$, resulting in a solid waste containing heavy metals and radioactive elements such as U, As, Fe, etc. The reaction is as follows:

HF (gases, radioactive elements) + KOH

$\Leftrightarrow KF + H_2O$

$2KF + Ca(OH)_2 \Leftrightarrow$

CaF_2 (solid, radioactive elements) +2KOH
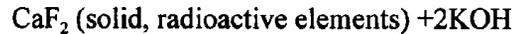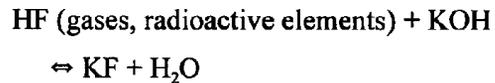
The above treatments give rise to two serious problems: one is the loss of the expensive fluoride element, and the other is the discarding of the final solid waste. A bipolar membrane cell can be used to solve these problems. The first step is the same as the above. The key point is that the KF produced in the first step is dissociated by a bipolar membrane cell to recover KOH for recycling. By means of a conventional electrolytic cell as shown in Fig.7, concentration of the recovered HF can be attained as high as 30–40%. Thus no additional $Ca(OH)_2$ is needed, and neither is any solid waste discarded.

In addition, the technologies based on a bipolar membrane can also be applied in the fields such as flue gas desulfurization, sodium alkali recycling in pulping and bleaching operations and ion-exchanger regeneration to control pollutant release and allow zero rejection [21–25].
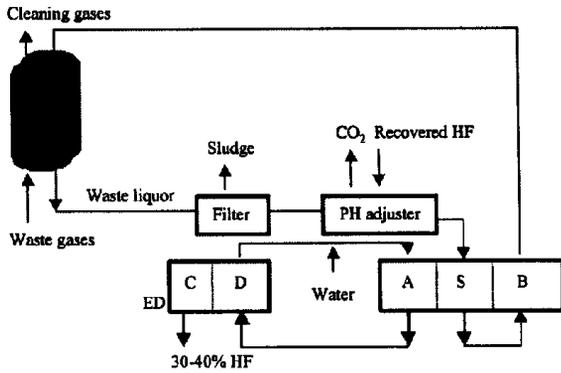
Fig. 7. Recovery of HF from waste water containing fluoride using a bipolar membrane cell and a conventional electrolytic cell. A, S and B: acid, salt and base compartment; C, D: concentrated, dilute compartment.

Fig. 8. Current efficiencies for citric acid production vs. time at $i = 100$ mA.cm^{-2}.

4. Biology and biochemical engineering applications

4.1. Production of organic acids

As we know, in the conventional production of organic acids, the following route is very common. The feed is fermented followed by filtration, and the filtered liquor is precipitated with lime followed by acidification with H_2SO_4 and again filtration to get the final products. The product obtained by this technique is usually at a low concentration, e.g., 0.2–1 N due to the limitation of the fermentation process, because the fermentation process typically operates at near neutral pH, this being maintained via addition of a suitable base. Increasing the product concentration significantly reduces the productivity of the fermentor due to product inhibition. In addition, large amounts of wastes are produced from the filtration and precipitation processes.

Bipolar membrane water splitting technology provides an ideal complement to the fermentation technology by removing the product acid while simultaneously providing an equivalent amount of base for use in adjusting the pH in the fermentor. The fermentor itself can now be operated at relatively low product concentrations
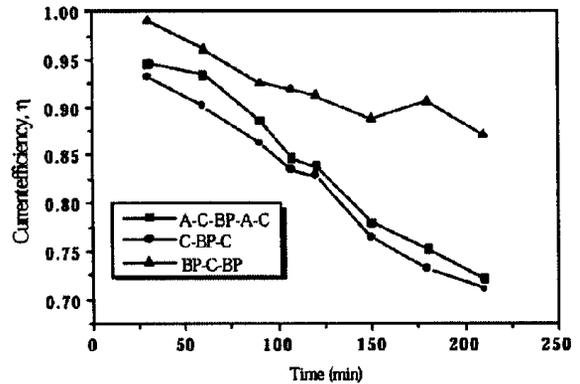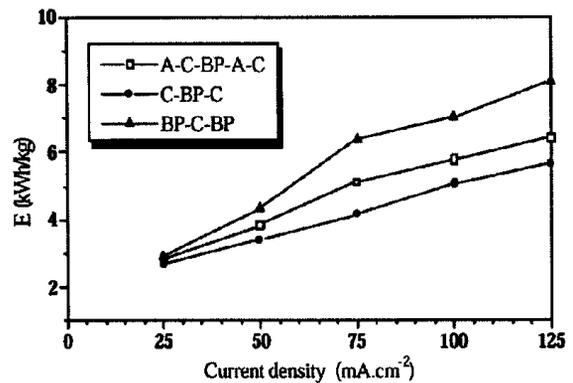

Fig. 9. Energy consumption for the production of citric acid production vs. current density.

to assure high productivity. As an added advantage, the recovered acid is usually at a significantly higher concentration (e.g., 4–6 mol.L^{-1}) so that the subsequent purification via crystallization or other techniques is relatively inexpensive. This technology has been used in several industries for producing lactic acid, citric acid, acetate acid, salicylic acid, etc. [26–32].

This process is not only dependent on cell configuration but also on the electrolyte and organic salt concentration. The current efficiency and energy consumption of citrate acid production is shown in Figs. 8 and 9 for three kinds
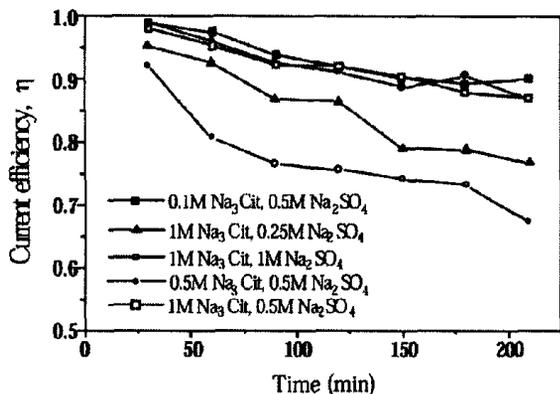
Fig. 10. Current efficiencies for citric acid production vs. time at $i = 100$ mA.cm^{-2} for the BP–C–BP unit.
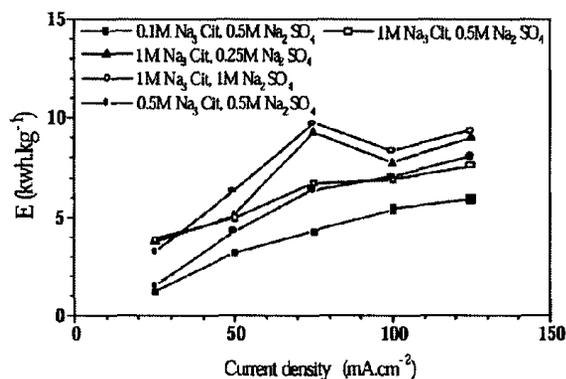

Fig. 11. Energy consumption for the production of citric acid vs. current density for the BP–C–BP unit.

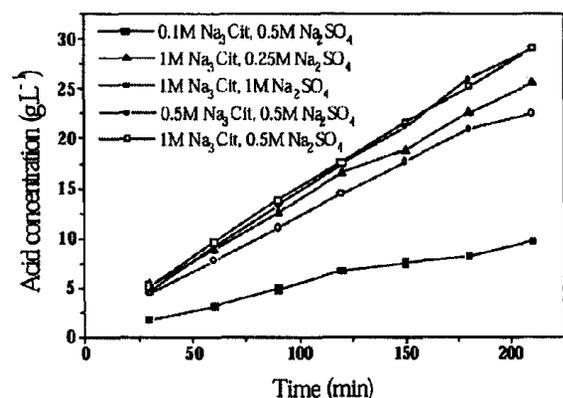Fig. 12. Time dependence of citric acid concentration in the acid compartment ($i = 100$ mA.cm^{-2}) for the BP–C–BP unit.

of basic cell configurations: A (anion membrane) –C (cation membrane)–BP (bipolar membrane) A–C, C–BP–C and BP–C–BP [33]. It is demonstrated that the magnitudes of current efficiency and energy consumption follow the analogous order as BP–C–BP < A–C–BP–A–C < C–BP–C, indicating that the BP–C–BP configuration seems to be a favorable one for the production of citrate acid [33]. If the BP–C–BP configuration is fixed, the optimum concentration range is 0.5–1.0 M for sodium citrate and 0.25–1.5 M for sodium sulfate from the viewpoint of energy consumption, current efficiency and acid concentration as shown in Figs. 10–12 [34].

4.2. Electro-acidification — production of soy protein isolates [31, 35–39]

A large proportion of the soya protein used in the food industry is in the form of protein isolates. Separation of proteins by isoelectric precipitation at the isoelectric pH range 4.2–4.6 is the recognized industrial process that involves five steps: extraction, precipitation, washing, resolubilization and drying. The disadvantages of this method include denaturation of protein on exposure to alkali and acid treatment, high ash content, and alteration of protein solubility after rehydration [31,40]. Local extremes in pH can cause irreversible denaturation of the proteins [41,42]. Bazinet et al. developed an electro-acidification technology using a bipolar membrane to precipitate soy proteins [35–39]. The protons generated by the bipolar membrane come into contact with the protein, bringing them to their isoelectric point, resulting in selective separation. Centrifugation can then be used as in the conventional process for separation of the proteins. To lower the pH of the protein solution, this solution was circulated on the cationic side of the bipolar membrane. The pH of the protein solution was lowered from 8.0 to 4.5 in a cell of 100 cm^2 effective electrode surface at a constant current of 25 mA.cm^{-2}. Lowering the pH to 4.5

allowed a precipitation of 95% protein. The chemical composition of bipolar membrane electrodialysed samples was demonstrated to be superior or equal to that the of commercial standards SUPRO-515,SUPRO-500 and SUPRO-600, with functional properties comparable to these standards [38,39]. After washing the precipitate, it was possible to resolubilize the proteins by reusing the sodium hydroxide generated on the anionic side of the bipolar membrane or by recirculating the precipitated protein solution on the anionic side during the acidification of another protein solution on the cationic side of the bipolar membrane. Separation of soya protein by bipolar membrane electrodialysis has specific advantages over the conventional isoelectric precipitation used industrially for the production of soybean protein isolates. This technology does not use any added acids or bases during the process to adjust the pH of the protein solution, and the chemical effluents generated during the process could be reused at different stages in the process. The water consumption is decreased by reusing the effluents generated, and the cell electrical energy consumption for protein precipitation is low (~0.3–0.7 kWh per kg of protein). In addition, the chemical composition of the electrodialysed samples was demonstrated to have a lower salt content than proteins separated by the conventional isoelectric process [31].

This process can also be used for the inhibition of polyphenol oxidase in apple juice, the enzymatic browning of cloudy juice, and separating soybean proteins from other components without denaturing them [43–49]. The energy and electroacidification parameters will be affected by various factors such as the number of bipolar membranes, temperature and concentrations of both support electrolyte and soy protein [37,38]. Increasing the number of bipolar membranes (1–4 BPs) accelerates the electrochemical precipitation in a quasi-linear fashion while also increasing the electrical efficiency [37]. Increasing the temperature from 10–35°C

slows the precipitation of proteins by decreasing hydrophobic interaction, but the energy efficiency appears to be increased due to a decrease in duration of the procedure [37]. The KCl and protein concentrations have an important effect on the performance of bipolar membrane electroacidification. By increasing the protein concentration (from 15 to 60 $g.L^{-1}$) and the KCl concentration (from 0.06 to 0.24 M), the relative power consumption decreases by a factor of 5.7 (from 2.82 to 0.49 $kW.kg^{-1}$ of protein produced) [38].

5. Cleaning resources — bipolar accumulator (cell) [50,51]

Just as a theoretical potential of 0.828 is exhausted for water dissociation into 1 M acid and 1 M base by a bipolar membrane unit, an equal potential drop will be produced by neutralizing the equal acid and base. Generally, this part of energy is often discarded. But if a neutral reaction occurs in a bipolar cell, the energy can be accumulated by a couple of irreversible electrodes. Fig. 13 shows the discharging process of a bipolar battery, which is constructed with a bipolar membrane and a couple of electrodes. By circulating the acid into the cation side of the bipolar membrane and base into the anion side, the acid and base will diffuse into the middle of a bipolar membrane and neutralize at the junction, producing a net energy which can act as a source by a couple of irreversible electrodes. Ordinarily, one bipolar membrane unit produces about 0.4–0.8 V. But this value will increase with the application of some energy-increasing electrodes. For example, if an Ag/Ag_2O electrode is applied, the reaction in both the electrodes and standard potentials is as follows:
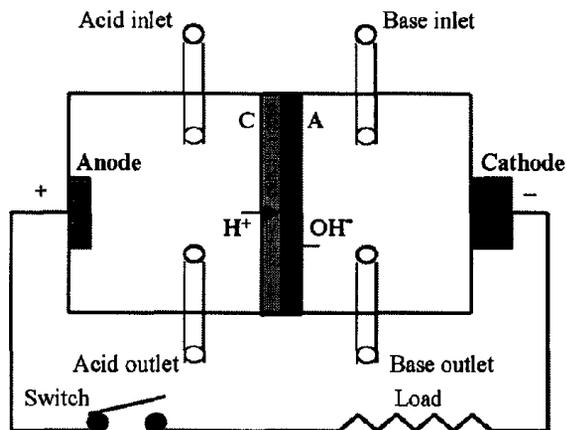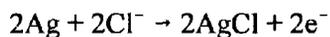
- Cathode reaction:
$Ag_2O + H_2O + 2e^- \rightarrow 2Ag + 2OH^-$;
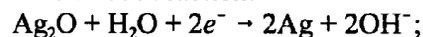
       theoretical potential: 0.344 V

Fig. 13. Discharge process of a bipolar membrane cell.

Fig. 14. Charge process of a bipolar membrane cell.

Table 1
Conventional energy-supply electrodes

Cathode	Anode
AgCl	Ag/Fe/H$_2$/Po/Zn/Zn(Hg)
AgO	Ag/[Co(NH$_3$)$_6$]$^{2+}$/Fe/[Fe(CN)$_6$]$^{4-}$/Ni
Ag$_2$	Ag//Fe/[Fe(CN)$_6$]$^{4-}$/Pb/Zn
Co^{3+}	Ag/[Fe(CN)$_6$]$^{4-}$/H$_2$/Pb/Zn
Fe^{3+}	Ag/[Co(NH$_3$)$_6$]$^{2+}$/[Fe(CN)$_6$]$^{4-}$/ H$_2$/Pb
O$_2$	Cr^{2+}/Ti^{3+}/ H$_2$/Pb/Zn(Hg)
Cl$_2$	Cr^{2+}/Ag/Ti^{3+}/ H$_2$/Zn(Hg)

• Anode reaction:

$$2Ag + 2Cl^- \rightarrow 2AgCl + 2e^-$$

   theoretical potential: -0.222 V

• Neutral reaction:

$$2H^+ + 2OH^- \rightarrow 2H_2O$$

   theoretical potential: 0.828 V

• Total: 0.95 V

Obviously, if this kind of electrode is used, an additional potential drop of 0.122 V can be supplied. Conventional energy-supply electrodes are shown in Table 1.
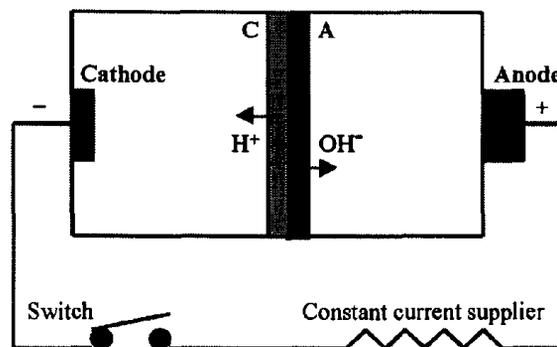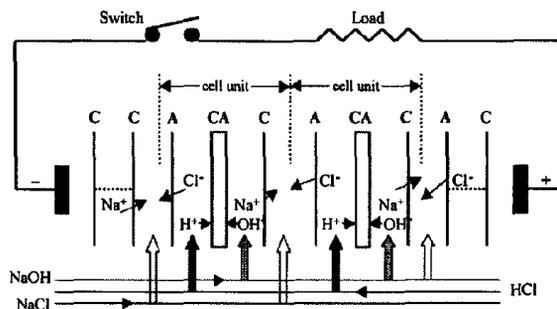

Fig. 15. Illustration of a bipolar membrane battery having a plurality of unit cells for the production of electrical energy (100 unit, 40–80 V, 60 kW/m^2).

A bipolar membrane battery can be recharged if it is used up. The charging process is completely the same as the water dissociation by additionally supplying energy as shown in Fig. 14. However, the sign of the electrode is reversed, just as the relationship of a source battery and an electrolytic cell.

The above unit can be accumulated into a bipolar membrane stack for battery for practical applications because a single unit produces so little voltage. For example, if 100 units construct a stack as in Fig. 15, it is expected to attain 40–80 V with an output power of 30–60 kW/m^2 [50], which can provide a commercially useful, regenerative process for electrical energy storage

to permit leveling of power loads. One of the greatest advantages is that the cell can provide energy with waste acid and base.

6. Conclusions

Bipolar membrane electrodialysis technology is an environmentally friendly technology with a wide-ranging application potential. We have attempted to give a general background on the new technology and use practical examples covering the many cell configurations and operating techniques to devise new processes or improve existing ones. The applications have been classified under the broad categories of chemical manufacture/resources recovery/cleaning separation/biology, etc. From the illustrated examples, it is easily observed that a bipolar membrane-based process has a number of significant advantages:

- The process is simple in concept. The only pretreatment needed is filtration to remove insoluble material, sludge, etc;
- It generates only the desired product into the purified and concentrated form;
- It can reduce or eliminate the pollution caused by conventional production such as production of organics, electroacidification of soy protein, etc.;
- It can do the job which cannot be done by conventional methods such as separation of ions with the same valence and sign;
- The recovery process of acid eliminates the costs associated with the purchase and utilization of neutralization chemicals;
- The process significantly reduces the amount of waste disposal while recovering valuable chemicals.

Technologists and researchers should, therefore, give serious consideration to using this technology in applications involving process improvements or resource recovery/recycling.

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