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Electrodialysis processes with bipolar membranes (EDBM) in environmental protection—a review

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Abstract

Electrodialysis with bipolar membranes (EDBM) has recently gained increasing attention for the production of acids and bases from the corresponding salt solutions. This process can be very energy-efficient and has a multitude of interesting applications. The intention of this paper is to give a brief overview and technical advantages with the practical applications of EDBM in environmental protection including waste recovery and cleaning production. © 2002 Published by Elsevier Science B.V.

Keywords: Bipolar membrane; Water dissociation; Electrodialysis; Waste recovery; Cleaning production

1. Introduction

A bipolar membrane (BM) is a laminar functional composition of membrane that at least consists of a layer ion-exchange structure composed of a cation selective membrane (with negative fixed charges) and an anion selective membrane (with positive fixed charges) (Heinz and Rachid, 2001; Francesco and Rosignano, 1998; Simons and Bay, 1993; Bauer et al., 1988). Just the same as that the discovery of semiconductor N–P junctions brings about the invention of many new semiconductor instruments, this composition of anionic and cationic exchange layer brings

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about many novelties (Bauer et al., 1988; Xu et al., 1998, 2000, 2001; Xu, 2001), such as separation of mono- and divalent ions, anti-deposition, anti-fouling, water dissociation, etc. Particularly, electrodialysis with bipolar membrane (EDBM) technology, which is regarded as the one of most promising fields, has acted as a new growth point in electrodialysis industries due to its superiority to conventional water electrolysis in the points (Xu et al., 1999; Nagsubramanian et al., 1977):

- no gases generated and low running cost (water is directly dissociated to H^+ and OH^-);
- low initial cost and space-saving (no electrode is needed in the repeating cell);
- no oxidation and/or reduction species that may produce undesirable products (no electrochemical reaction).

However, and as for all the processes, EDBM has its limitations (Mani, 1991; Pourcelly and Gavach, 2000). Firstly, the performances of a water splitter are controlled by the permselectivities of the individual component membranes and by diffusive transport. Due to the leakage of the individual membrane, the undesired diffusion processes such as cations through anion membrane and anions through cation membranes reduce the current efficiency. Consideration must also be paid to water transport through membranes, which in general limits the concentration level of the acid and base produced. Apart from these limits, EDBM process has a relatively strict request to the feed conditions. A pre-treat of solutions is necessary to remove multivalent cations and organic pollution in case of membrane swelling and metallic hydroxides precipitation. Nevertheless, some limits can be overcome by improving membrane quality or the cell configurations (Xu et al., 2000; Xu and Yang, 2001a). If the final product is not the strong acid or base, the concentration of strong acid or base is also not so important.

Due to the ability to dissociate water into hydronium ions and hydroxyl ions, a BM has been found many applications in industries and daily life, such as chemical production and separation, biochemical engineering, environmental conservation etc. (Pourcelly and Gavach, 2000; Xu and He, 2000; Blackburn, 1999). The involvement of a BM in these fields can significantly change the features of the conventional processes and eliminate the potential contamination to the environment. The main purpose of this paper is to give an overview to the potential applications of BM-based technologies in cleaning production and resources/power recovery.

2. General description of water splitting with a bipolar membrane

The principle of water splitting (EDBM) is illustrated in Fig. 1. A BM is placed in the middle of the cell, which has two electrodes at the two sides and contain a salt solution. If a potential difference is established between the two electrodes, any salt at the interface of BM is removed during current flow, the cations migrating in the direction of the current through the cation layer to cathode and the anions flowing in the opposite direction to the other side solution. When all the salt ions initially contained are removed from the membrane, the transport of electrical

charge through the membranes can only be accomplished by protons and hydroxyl ions and thus water dissociation commences (Mani, 1991; Kedem and Warshawsky, 1994; Mazrou et al., 1997). Due to the dissociation equilibrium, protons and hydroxyl ions removed from the system will continuously be replenished. The net results are that an alkaline solution is formed on the anion-exchange side and an acid solution on the cation exchange side of a BM.

3. Cleaning production

As described above, BMs are able to electrically separate water into hydronium and hydroxyl ions. When used in conjunction with conventional cation and/or anions membrane, they provide a low energy and simple process for cleaning production as described in the following.

3.1. Production of acid and base from the salt solution (Mazrou et al., 1997, 1998; Gineste et al., 1996)

It is a well-known technology originated from BM dissociation. In this process, there are two kinds of cell arrangements: one is two-compartment unit and another is three-compartment as shown in Fig. 2(a) and (b). Two-compartment is simple in structure, but the base produced from cathode has a tendency to transport to the acid compartment through anion membrane and neutralize the acid produced from water dissociation and thus decreased the current efficiency. This disadvantage is overcome by a three-compartment. 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 the produced acid and base can be attained as high as 6 N by using this configuration (Gineste et al., 1996). In China, this new technology has been used in the industry to manufacture silica acid (H_2SiO_3) from Na_2SiO_3 .

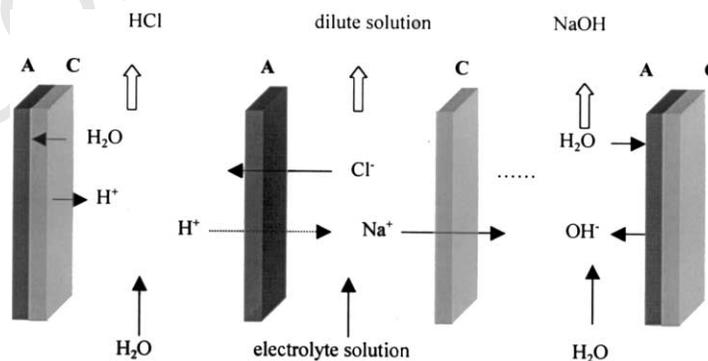


Fig. 1. Schematic representation of water splitting on a bipolar membrane.

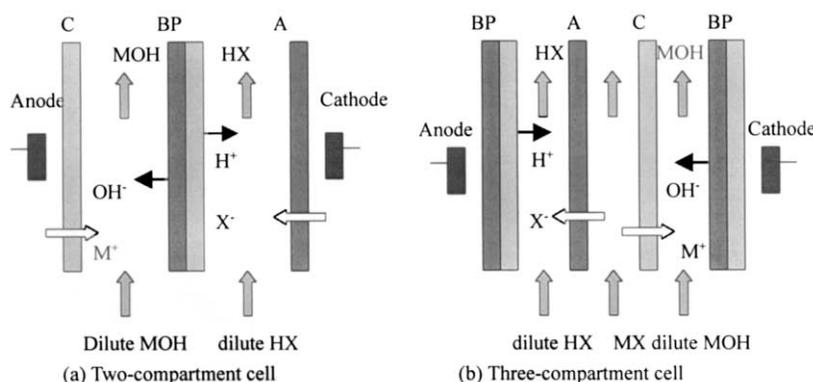


Fig. 2. Fundamental cell arrangement for production acid and base from the corresponding salts. C, cation membrane; A, anion membrane; BP, bipolar membrane; HX, acid; MX, salt; MOH, base.

Compared with the conventional ion exchange method, the energy consumption can be decrease from 1 over to 0.6 kWh/kg of product at the current density 10–12 mA/cm² (Lin, 2001).

3.2. Production of organic acids

As shown in Fig. 3, in the conventional production of organic acids, the following route is very common. The feed is fermented followed by a filtration and the filtered liquor is precipitated with lime followed by acidification with H₂SO₄ and again-filtration to get the final products. The product obtained by this technique is usually at low concentration, e.g. 0.2–1 N due to the limitation of fermentation process. Since 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 fermenter due to product inhibition. In addition, large amounts of wastes produced from the filtration and precipitation processes.

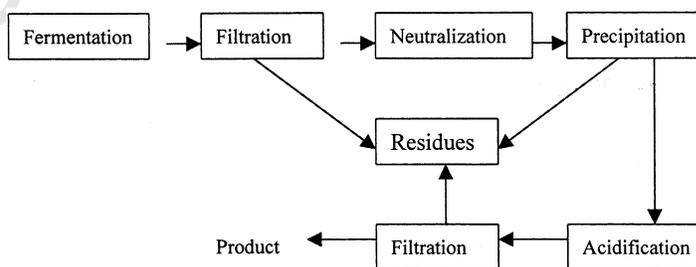


Fig. 3. Schematic drawing of a conventional process for producing organic acid. Enzymatic Fermenter.

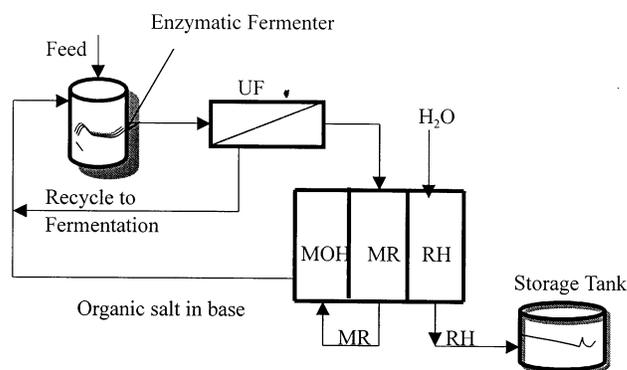


Fig. 4. Amino/organic acid production based on both fermentation and bipolar membrane processes.

BM 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 fermenter. The fermenter itself can now be operated at relatively low product concentrations to assure high productivity. As an added advantage the recovered acid is usually at a significantly high concentration (e.g. 4–6 mol/l) 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. (Xu and Yang, 2001a,b; Lee et al., 1998; Trivedi et al., 1997; Alvarez et al., 1997). A typical flow sheet of the combined fermentation and water dissociation process was shown in Fig. 4.

This process is not only dependant on cell configuration but on the electrolyte and organic salt concentration as well (Xu and Yang, 2001a,b). The current efficiency of citric acid production is shown in Fig. 5 for three kinds of basic cell configurations: A (anion membrane)–C (cation membrane)–BM–A–C, C–BM–C

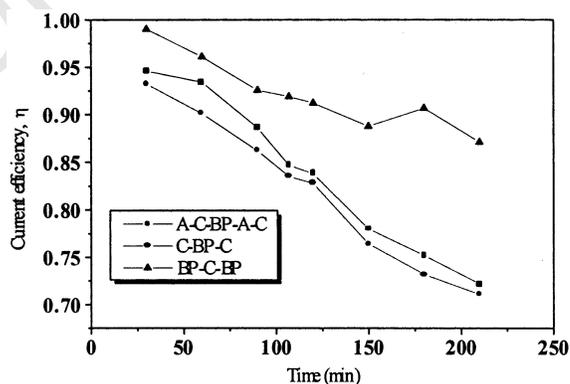


Fig. 5. Current efficiencies for citric acid production versus time at $i = 100 \text{ mA/cm}^2$.

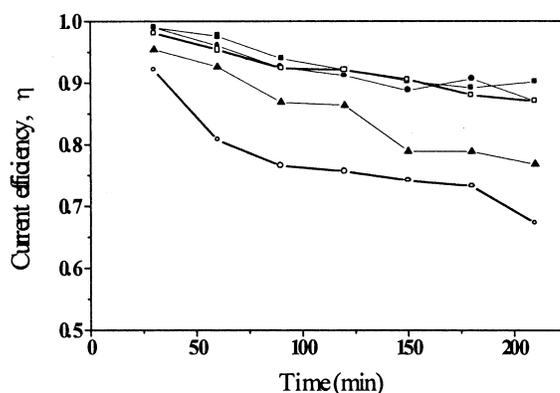


Fig. 6. Current efficiencies for citric acid production vs. time at $i = 100 \text{ mA/cm}^2$ for BP-C-BP unit. ■, 0.1 M Na₃Cit, 0.5 M Na₂SO₄; ●, 0.5 M Na₃Cit, 0.5 M Na₂SO₄; ▲, 1 M Na₃Cit, 0.25 M Na₂SO₄; □, 1 M Na₃ Cit, 0.5 M Na₂SO₄; ○ 1 M Na₃Cit, 1 M Na₂SO₄.

and BM-C-BM (Xu and Yang, 2001a). It is demonstrated that the magnitudes of current efficiency and energy consumption follow the analogous order as BM-C-BM < A-C-BM-A-C < C-BM-C, indicating that BM-C-BM configuration seems to be a favorable one for the production of citrate acid (Xu and Yang, 2001a). If the configuration of BM-C-BM 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. 6 and 7 (Xu and Yang, 2001b).

3.3. Production of soy protein isolates (Bazinet et al., 1998, 1997a)

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 isoelec-

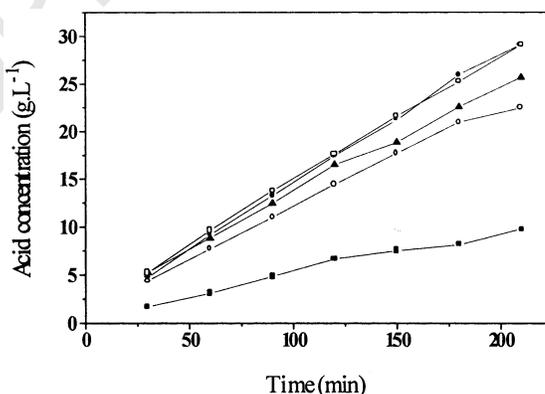


Fig. 7. Time dependence of citric acid concentration in the acid compartment ($i = 100 \text{ mA/cm}^2$) for BP-C-BP unit. ■, 0.1 M Na₃Cit, 0.5 M Na₂SO₄; ●, 0.5 M Na₃Cit, 0.5 M Na₂SO₄; ▲, 1 M Na₃Cit, 0.25 M Na₂SO₄; □, 1 M Na₃ Cit, 0.5 M Na₂SO₄; ○ 1 M Na₃Cit, 1 M Na₂SO₄.

tric pH range 4.2–4.6 is the recognized industrial process, which 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 (Bazinet et al., 1998; Nash and Wolf, 1967). Local extremes in pH can cause irreversible denaturation of the proteins (Kilara and Sharkasi, 1986; Fisher et al., 1986). Bazinet et al. developed an electro-acidification technology using a bipolar to precipitate soy proteins (Bazinet et al., 1997a). The protons generated by the BM 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 BM. The pH of the protein solution was lowered from 8.0 to 4.5 in a cell of 100 cm² effective electrode surface, at a constant current of 25 mA/cm². Lowering the pH to 4.5 allowed a precipitation of 95% protein. The chemical composition of BM electrodialed samples was demonstrated to be superior or equal to that of the commercial standards SUPRO-515, SUPRO-500 and SUPRO-600, with functional properties comparable to these standards (Bazinet et al., 1997a). After washing the precipitate, it is possible to resolubilize the proteins by reusing the sodium hydroxide generated on the anionic side of the BM, or by circulating the precipitated protein solution on the anionic side during the acidification of another protein solution on the cationic side of the BM. Separation of soya protein by BM electrodialed 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/kg of protein). In addition, the chemical composition of the electrodialed samples was demonstrated to have a lower salt content than proteins separated by the conventional isoelectric process (Bazinet et al., 1998).

The energy and electroacidification parameters will be affected by various factors such as the number of BMs, temperature and concentrations of both support electrolyte and soy protein (Bazinet et al., 1997b,c). Increasing the number of BMs (1–4 BMs) accelerates the electrochemical precipitation in a quasilinear fashion, while also increasing the electrical efficiency (Bazinet et al., 1997b). Increasing the temperature from 10 to 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 (Bazinet et al., 1997b). The KCl and protein concentrations have an important effect on the performance of BM electroacidification. By increasing the protein concentration (from 15 to 60 g/l) 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 of protein produced) (Bazinet et al., 1997c).

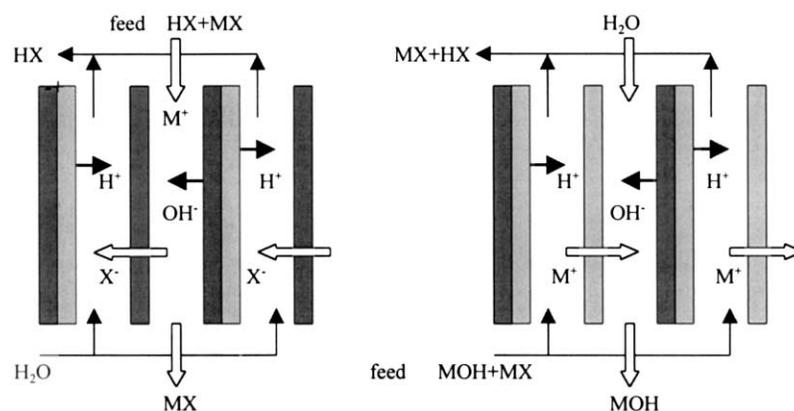


Fig. 8. Schematic drawing for acid and base recovery and purification unit. (a) Acid purification cell unit. (b) Base purification cell unit.

4. Resources and/or power recovery/recycling

4.1. Recovery/purification of inorganic acid and bases from the spent liquors (Chao et al., 1991; Graillon et al., 1996; Mani et al., 1998)

The application of a BM based process to purify acid and base stream is based on the recognition that the BM can act as a highly selective cation or anion membrane in a conventional electrodiagnosis-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; pure caustic soda from an NaOH/NaNO₃ mixture in the Ni/Cd battery manufacture; HCl and NaOH from ion exchange regeneration streams; sulfuric acid from aluminum anodizing baths; nitric acid from uranium processing operations; HNO₃ and NH₄NO₃ system 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 the free acid or base. When a BM is used in this manner, it provides an effective means for purifying acids and bases and can achieve product purification and concentrations that are not achievable via conventional electrodiagnosis, diffusion dialysis or ion retardation techniques. The cell configuration for acid recovery is shown in Fig. 8(a). The assembly is similar to a conventional electrodiagnosis except that the BMs replaced the conventional cation membranes. As shown in Fig. 8(a), the feed compartment bounded by the anion side of the BM and the anion membrane is fed with the impure acid stream contaminated with cations of metals such as Na, Fe, Cr, Cd, Al, Ti, etc. Water or dilute acid is fed to the product chamber bounded by the cation side of the BM and

the anion membrane. When a direct current is passed between the electrodes, hydronium ions from the BM are introduced into the product compartment. Simultaneously, the electric current causes the transfer of anions across the anion membrane to the product compartment and form acid. The concentration of acid in feed compartment is reduced as a result of the anion and net hydronium ion 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 feed compartment.

The cell configuration for base purification is similar to the above with cation membranes replacing the anion membranes as shown in Fig. 8(b), the purification process works in a manner analogous to the acid purification cell. The impure is introduced into the compartment bounded by the cation side of the BM 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 BM). Here they combine with the hydroxyl ions formed at the BM, yielding a purified base product.

Graillon et al. used this technology to treat the concentrated nitrate effluents from ammonium nitrate solution (Graillon et al., 1996). This treatment involved two steps in case of the leakage of ammonium through the membranes. The first is the ammonium stripping after neutralization of 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).

4.2. Recovery/purification of amino/organic acids and salts (Novalic and Kulbe, 1998; Grib et al., 1998; Yu et al., 2000a)

As shown in Fig. 3, precipitation is a key step for production of organic/amino acids by fermentation technique. However, in most cases, not all organic/amino acids or their salts can be extracted from this step due to the solubility or other factors, leaving a fairly large portion of organic/amino acids or their salts in the spent liquor. For example, during the production of monosodium glutamate (NaG), about 20% glutamate remains in the waste liquor. To recover this part of NaG, two methods are generally available, one is the ion exchange method and the other is the evaporation to concentrate the liquor. Both methods demonstrated many shortcomings: the former needs large quantities of bases and acids for the regeneration of resins, moreover the operation is batchwise; and the latter consumes large quantities of energy and decrease the purity of the corresponding products due to the accumulation of the impurities. The most attractive measure to treat this problem is using a BM technique. Fig. 9 demonstrates a electrolytic unit based on a BM for this purpose, which consist of two pieces of BMs and one piece of anion membrane, separating the unit into two cells. The left cell passes the stripping water while the right cell the feed containing NaG. Following the analogous process to

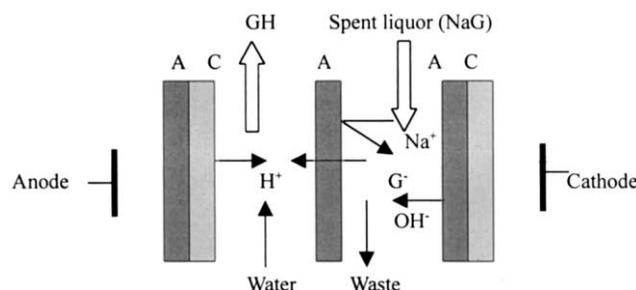


Fig. 9. Schematic diagram for recovery monoacid glutamate from the spent liquor by a BP process. A, anion membrane layer, C, cation membrane layer, G, glutamate ion.

the above, The recovered acids (GH) was obtained in the left chamber and the base in the right one, which can be recycled to the fermentation process to adjust the pH value in the liquor. Compared the previously mentioned processes, this new technique reduces the environmental contamination to a significant extent. It not only saves the operation steps and energy consumption, but makes the process continuous as well.

4.3. Flue gases (CO_x , NO_x and SO_x) cleaning and recovery (Liu et al., 1978)

Flue gases, such as SO_x , CO_x and NO_x , etc. emission from industrial sources that burn impurity fuels is a major environmental problem in the world. It bring serious problem to our environment such as acid rain resulted from sulfur dioxide, warm effect resulted from carbon dioxide and light pollution from nitrogen oxide. So people must give a serious consideration to this problem. Though there are many ways that are used in the in situ industries, BM provide a simple and economical treatment to these problems. The principle and process are illustrated based on sulfur oxide as shown in Fig. 10. Obviously, it is a two-compartment electrochemical water splitting unit containing only cation and BMs. The SO_2 is first removed from

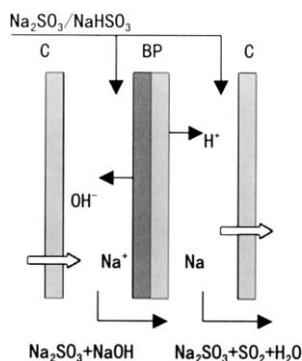


Fig. 10. Two-compartment conversion unit for $NaHSO_3$.

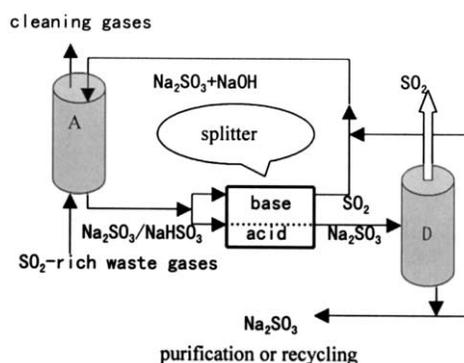
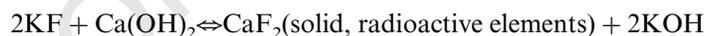


Fig. 11. Soxal™ flue gas desulfurization process. A, absorber, D, desorber.

the stack gases by means of an alkaline scrubbing solution. The spent solution is then regenerated in this cell into alkaline and acid sulfate. The former is recycled at the initial stage and the latter was desorbed and SO_2 is liberated and recovered for further processing. The results showed that an excellent current efficiency of 85% could be obtained, which provide a good background for industrial application. An excellent example is the Soxal flue gas desulfurization process as shown in Fig. 11. This principle can also be applied to CO_x or NO_x systems.

4.4. 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 precipitating with $\text{Ca}(\text{OH})_2$, resulting a waste in solid containing heavy metals and radioactive elements such as U, As, Fe, etc. The reaction is as follows:



The above treatments give rise to two serious problems: one is the loss of expensive fluoride element and other is the discarding of the final solid waste containing radioactivity. A BM cell can be used to solve these problems. The key point is that the KF produced in first step is dissociated by a BM cell to recover KOH for cycling. By means of a conventional electrolytic cell as shown in Fig. 12, concentration of the recovered HF can be attained as high as 30–40% (Xu and He, 2000). So no additional $\text{Ca}(\text{OH})_2$ is needed and neither any solid waste discarded.

4.5. Recovery cupric from the dilution waste (Xu and He, 2000)

As shown in Fig. 13, the feed containing cupric is circulated from compartment 1, and the extractant organic phase containing ion exchange resin is filled in

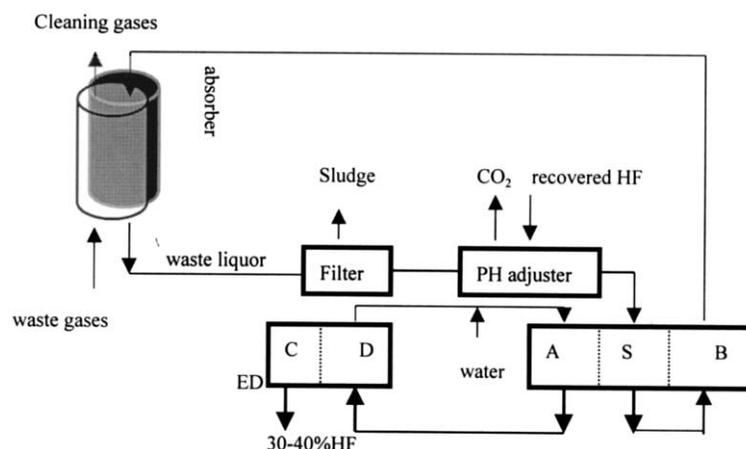


Fig. 12. Recovery of HF from water containing fluoride using a bipolar membrane cell and a conventional electrolytic cell. A, S and B-acid, salt and base compartment; C, D-concentrated, dilute compartment.

compartment 2. When a voltage is applied, cupric ions and other cations will transport through a cation membrane from compartment 1 to 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 the compartment 3 at the right, where back-extraction takes place and cupric ion are released and transport to the compartment 4 under the condition of acidity produced from the water dissociation. And thus, the net result is that if the feed is circulated from compartment 1, copper-rich aqueous phase can be obtained in compartment 4. No additional extractant is necessary in the process and neither is the conventional back-extraction is needed. The operation is a combination of ion exchange, extraction and water dissociation. Ion exchange resin provides a decisive role in the

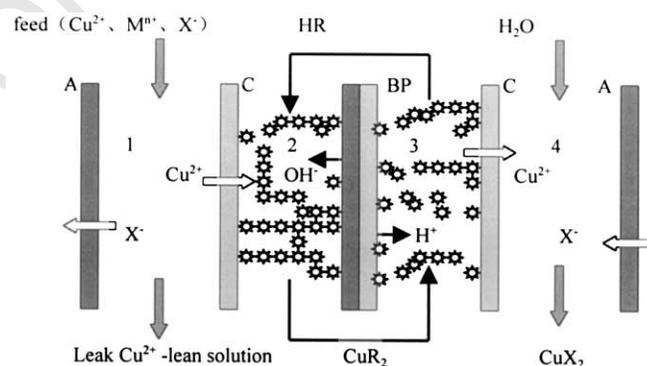


Fig. 13. Concentrating cupric ions by bipolar electro-extraction. HR-extractant and \star represents ion exchange resin.

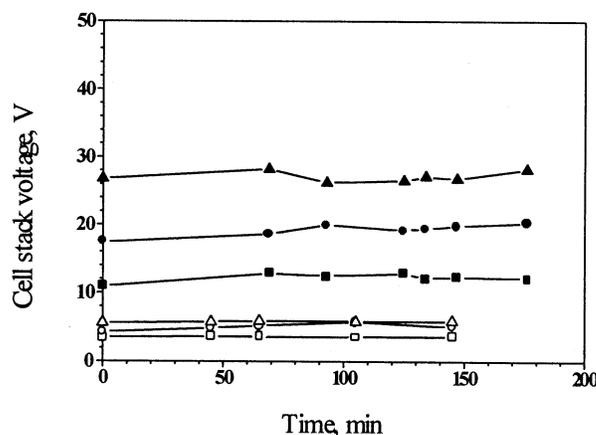


Fig. 14. Cell voltage changes at various current densities 50 (square), 80 (circle) and 100 (triangle) mA/cm², respectively, for electroextraction. Solid symbols for D001 porous resin and open symbols for 001*7 resin.

process because it not only acts a bridge for the exchange between ions and organic phase but also increases the conductivity of organic phase and thus decreases the operation voltage. We use two kind of ion resin produced in Nankai Chemical Plant (China): D001 porous cation resin and 001*7 gel cation resin for recovering copper from its dilute solution (Xu and He, 2000). We found that the voltage of the cell stack, whose configuration is shown in Fig. 13, was strongly affected by the resin. As shown in Fig. 14, 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/cm², 0.70–0.84 at 80 mA/cm² and 0.44–0.65 at 100 mA/cm² for D001 porous resin, and 0.88–0.95 at 40 mA/cm², 0.67–0.78 at 80 mA/cm² and 0.56–0.62 at 100 mA/cm² for 001*7 gel resin. Therefore, an average efficiency 90% can be achieved if the process is operated below 50 mA/cm² by using gel resin.

4.6. Recycle of pickling waste stream

Pickling of mines with inorganic acids such as H₂SO₄, HCl, HNO₃ or HF acid is one of the key steps in manufacturing of corresponding metals or metal oxide. This pickling process is usually accomplished by precipitation and leaving large quantities of spent liquor. Though these liquor can be circulated, the accumulation of metal ions (especial ones with high valence) in the solution will result in a decreased efficiency of the pickling agent and thus the eventual disposal is necessitated. This disposal of spent liquor has posed a problem in the whole metal finishing industry for a very long time and has prompted industries to give serious consideration to recover acid from products that are now going to wastes. Over the history of this problem, different methods of dealing with the spent pickling solutions have been

applied including direct disposal and neutralization. Of course, both of them are passive and not advisable (Xu and Yang, 2001). Electrodialysis with a BM provides an attractive method to circulate the stream and recover the metal without any disposal. Take the common stream containing HNO_3 , HF , Fe^{3+} , Cr^{3+} , Ni^{2+} as an example, the processes include the neutralization with base such as KOH , followed by a precipitation to get $\text{Fe}(\text{OH})_3$, $\text{Cr}(\text{OH})_3$, $\text{Ni}(\text{OH})_2$, etc. (Fig. 15). The filtrate is concentrated by a conventional electrodialysis. The stream from dilute compartment can be circulated to the filtration step, while the concentrated stream goes into a BM splitter and is dissociated into the corresponding acid and base. The produced acid is circulated at the initial pickling stage and the base for the neutralization. So the whole system discards nothing and the only necessities are the acid in the initial pickling and the base in the neutralization. Additional acid is not necessary.

4.7. Power production from waste acid and base streams

Just as a theoretical potential of 0.828 V is exhausted for water dissociation into 1 mol acid and 1 mol base by a BM unit at 25 °C (Strathmann et al., 1997; Strathmann and Koops, 2000), an equal potential drop will be produced by reacting 1 mol acid and 1 mol base. Generally, this part of energy is often

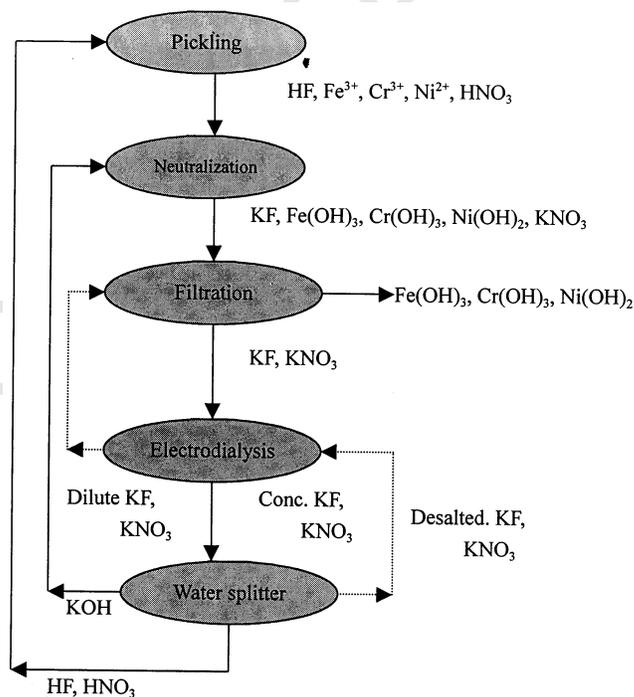


Fig. 15. Recycle of pickling waste stream.

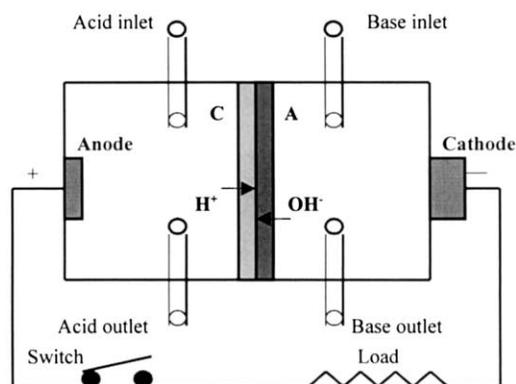


Fig. 16. Discharge process of a bipolar membrane cell.

discarded. But if a neutral reaction occurs in a EDBM cell, the energy can be accumulated by a couple of irreversible electrodes. Fig. 16 shows the discharging process of a BM battery, which is constructed with on BM and a couple of electrodes. By circulating the acid into the cation side of the BM and base into the anion side, the acid and base will diffuse into the middle of a BM and react at the junction, producing a net energy, which can act as a source by a couple of irreversible electrodes. Ordinarily, one BM unit produces about 0.4–0.8 V (Walther and Skaneateles, 1982; Zholkovskij et al., 1998).

A BM battery can be recharged if it used up. The charging process is completely the same as the water dissociation by additionally supplying energy as shown in Fig. 17. However, the signal of the electrode is reversed, just as the relationship of a source battery and an electrolytic cell.

The above unit can construct a BM stack for battery for practical applications because single unit produces so small voltage. For example, if 100 units construct a stack like Fig. 18, it is expected to attain 40–80 V with output power 30–60 kW/m². Of course this magnitude of power can act as energy supply for daily life. The one of the most advantages is that the cell can provide energy with wastes acid and base.

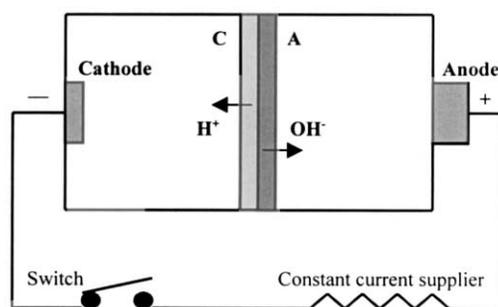


Fig. 17. Charge process of a bipolar membrane cell.

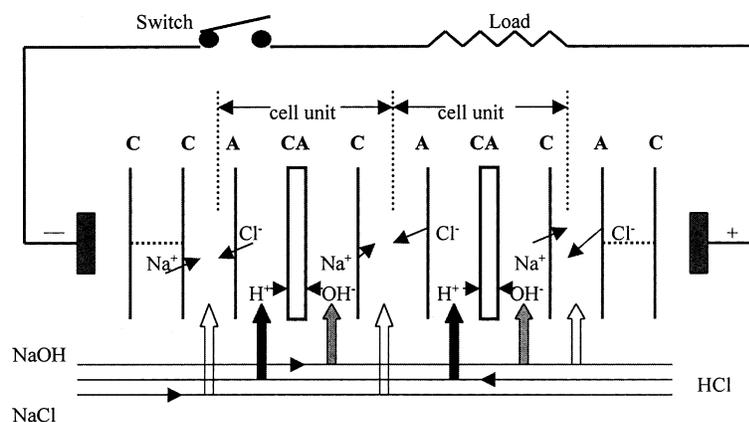


Fig. 18. Illustration of a bipolar membrane battery having a plurality of unit cells for the production of electrical energy (100 unit, 40–80 V, 60 kW/m²).

5. The economic and practical implications of EDBM in cleaning production and recovery

A universal valid prediction on economic analysis is hardly possible. Total process in EDBM may vary widely depending on location, capacity, individual application and so forth. Generally speaking, the aim of the process is the production of an acid or a base or both, or treatment of an industrial effluent as mentioned in the above sections. In these applications, EDBM is often competing directly with conventional process such as ion-exchange, electrolysis and chemical or electrochemical separation and conversion processes (Nagsubramanian et al., 1977; Strathmann and Koops, 2000).

The process costs in EDBM are determined to a large extent by the membrane properties, the feed condition and the required product quality as well as process and equipment design parameters such as the stack construction, the operating current density, etc. However, another parameter affecting the process costs is the membrane price. Since there is no large scale membrane production today, the prices of commercially available BMs for laboratory or pilot plant quantities are accordingly high (Strathmann and Koops, 2000) (this is also the reason why there are very few large-scale commercial installations of EDBM nowadays). The EDBM cost considerations in some implications of laboratory or industrial scale in cleaning production and recovery are accumulated in Table 1 (Pourcelly and Gavach, 2000; Siebolder et al., 1995; Yu et al., 2000b; Novalic et al., 2000).

6. Summary

The electro dialysis with a BM provides a new method for cleaning production resources recovery. In this paper, we have attempted to give a general background

Table 1
The process characteristics and economics of EDBM in some implications in cleaning production and recovery are accumulated in table

Application field	Scale	Process characteristics	Economics estimation	Reference
Recovery of HF and HNO ₃	Industrial plant, aqualytics system	Three compartment EDBM; membrane area 3×10^5 m ² ; BM life-time: 2 years; recovery ratio: 90% for HF, 95 for HNO ₃ ; time of production: 8000 h/year	Total investment: 2 950 000 US\$; operating profits: 1 620 000 US\$; total operating costs: 750 000 US\$; profits per year: 870 000 US\$	Pourcelly and Gavach, 2000
Recovery of NaOH from a stream containing Na ₂ SO ₄	Semi-industrial pilot	Membrane area: 0.5 m ² ; feed rate: 5 l/h; feed concentration Na: 22 g/l; current applied 900 A/m ² ; current yield: 82%; product NaOH concentration: 1 M	Energy consumption: 5.0 kWh/kg NaOH	Pourcelly and Gavach, 2000
Recovery of NH ₃ and HNO ₃ from a stream containing NH ₄ NO ₃	Semi-industrial pilot	Membrane area: 120 m ² ; feed concentration NH ₄ NO ₃ : 250 g/l; current applied 1000 A/m ² ; desalination rate: 97%; time of production: 8000 h/year	Total cost: 0.34 US\$ per kg of NaNO ₃	Pourcelly and Gavach, 2000; Graillon et al., 1996
Recycling of dimethyl isopropyl amine in the production of aluminum casting molds	Semi-industrial pilot	Membrane area: 0.3 m ² ; feed concentration amine sulphate: 1 M; current applied 800 A/m ² ; current yield: 30–70%; time of production: 8000 h/year	Energy consumption: 2.5–5.0 kWh/kg amine	Pourcelly and Gavach, 2000
Flue gas desulphuration	Industrial plant, Soxal™ process	Three compartment EDBM; membrane area 560 m ² ; cell voltage 2.0 V at 1000 A/m ² ; current efficiency: 86%, 7200 h/year; two compartment EDBM; membrane area 5000 m ² ; cell voltage 1.7 V at 1000 A/m ² ; current efficiency: 92%, 7200 h/year	Three compartment EDBM: energy consumption 1400 kWh/ton NaOH; two compartment EDBM: energy consumption 1120 kWh/ton NaOH	Mani, 1991; Pourcelly and Gavach, 2000; Liu et al., 1978

Table 1 (continued)

Application field	Scale	Process characteristics	Economics estimation	Reference
Recovery of gluconic acid from sodium gluconate	Pilot scale	Two compartment EDBM; membrane area 0.19 m ² ; elementary cell voltage 2.2 V at 415 A/m ² ; conversion ratio: 98.3%; Na Faradic yield 85.4%	For a plant of 10 000 ton/year: total costs: 2.5 million US\$; membrane replacement: 0.03 US\$ per kg of Na-gluconate; recovery chemicals: NaOH: 0.5 million US\$; gluconic acid: unknown	Pourcelly and Gavach, 2000
Recovery of methanesulphonic acid (MTA) from sodium methanesulphonate (MTS) solutions	Industrial plant (Italy)	Three compartment EDBM; membrane area 64 m ² ; elementary cell voltage 2.26 V at 800 A/m ² ; methanesulphonic conversion ratio: 95%; concentration: MTS, 250; MTA, 100; NaOH, 80 g/l	Total investment: 700 000 US\$; total costs per ton MTA: 354 US\$; The market price of MTA: 5500 US\$/ton	Pourcelly and Gavach, 2000
Recovery of an amino acid from a fermentation broth	Industrial plant, aqualytics system	Three compartment EDBM; membrane area 3 × 180 m ² ; BM life-time: 2 years; concentration of organic acid 4–6 M; time of production: 8000 h/year	No information available	Pourcelly and Gavach, 2000; Grib et al., 1998
Production of lactic acid from a fermentation broth	Industrial plant	Two compartment EDBM; membrane area 280 m ² ; current yield: 60%; conversion ratio: 96%	BM costs: 0.12 US\$ per kg and energy consumption: 1 kWh/kg of lactic acid	Pourcelly and Gavach, 2000; Lee et al., 1998; Siebolder et al., 1995
Regeneration of camphorsulphonic acid	Pilot-scale (France)	Three compartment EDBM; BM area: 0.14 m ² ; current density 500 A/m ² ; Faradic yield: 7%; salt conversion: 98.5%; final acid concentration: 0.8 M	Energy consumption: 3000 kWh/ton of products	Pourcelly and Gavach, 2000

Table 1 (continued)

Application field	Scale	Process characteristics	Economics estimation	Reference
Production of vitamin-C (Ascorbic acid H Asc) from sodium ascorbate (NaAsc)	Lab scale and semi-industrial pilot	Two Compartment EDBM; current density 1000 A/m ² ; current efficiency: 75% acid concentration: 1 M	Energy consumption: 1.4–2.3 kWh/kg Hasc.	Pourcelly and Gavach, 2000; Yu et al., 2000b; Novalic et al., 2000
Production of citric acid	Pilot scale (China)	Two compartment EDBM; BM area: 0.004 m ² ; current density 1000 A/m ² ; current efficiency: 70% acid concentration 30 g/l	Energy consumption: 2–5 kWh/kg of citric acid	Xu and Yang, 2001a,b; Novalic and Kulbe, 1998
Production of silicic acid	Industrial pilot	Two compartment EDBM; elementary cell voltage 2.5–4 V at 100–200 A/m ² current density; current efficiency: 55–75%; acid concentration: 6–10%	Energy consumption: 0.6 kWh/kg of product (6–10%).	Lin, 2001
Production of salicylic acid	Laboratory pilot	Three compartment EDBM; Tokuyama BM; elementary cell voltage 30 V at 750 A/m ² current density; current efficiency 80–90% at 40 °C; acid concentration: 4.5 (maximum) g/l	Energy consumption: 15–20 kWh/kg of product	Alvarez et al., 1997
Conversion of sodium acetate to acetic acid	Pilot scale	Five compartment EDBM; BM area 0.008 m ² ; 0.5 M sodium acetate: current efficiency: 99.9% and acid concentration: 1 M; 1.0 M sodium acetate: current efficiency: 96.8% and acid concentration: 1.5 M	Energy consumption: 1.3–2.0 kWh/kg (0.5 M sodium acetate) and 1.5–2.2 kWh/kg (0.5 M sodium acetate) of product	Trivedi et al., 1997; Yu et al., 2000a

on the new technology, and using practical examples, covered the many cell configurations and operating techniques that can be used to devise new processes or improving existing ones. The most important thing of these processes exists that they can bring about a cleaning production and separation when they are introduced in the traditional industries.

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

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