Contents

	PART I ELECTRICALLY DRIVEN MEMBRANE PROCESSES	
Chapter 1	Basis of Electromembrane Processes	3
• .	ROBERT E. LACEY	
Chapter 2	Physiochemical Aspects of Electromembrane Processes	21
	THOMAS A. DAVIS AND GEORGE F. BROCKMAN	
Chapter 3	Engineering and Economic Considerations in Electro- membrane Processing	39
•	EVERETT L. HUFFMAN AND ROBERT E. LACEY	
Chapter 4	Electromembrane Processing of Cheese Whey	57
	RICHARD M. AHLGREN	
Chapter 5	Electromembrane Processes for Recovery of Constituents from Pulping Liquors	71
	RICHARD M. AHLGREN	
Chapter 6	Concentration of Electrolytes with an Electromembrane Process Prior to Evaporation	83
	Tadashi Nishiwaki	
	PART II PRESSURE-DRIVEN MEMBRANE PROCESSES	
Chapter 7	Principles of Reverse Osmosis	109
	CHARLES E. REID	
	·	ix

•	Contents
	Contents

Chapter 8	Theory and Practice of Reverse Osmosis and Ultrafiltration
	H. K. Lonsdale
Chapter 9	The Costs of Reverse Osmosis
	ROBERT E. LACEY
Chapter 10	Reverse Osmosis in the Food Industry
	R. L. MERSON AND L. F. GINNETTE
Chapter 11	Applications for Reverse Osmosis in the Pulp and Paper Industry
	AVERILL J. WILEY, A. C. F. AMMERLAAN, AND G. A. DUBEY
Chapter 12	The Treatment of Industrial Wastes by Pressure-Driven Membrane Processes
	ROBERT W. OKEY
Chapter 13	Gas Permeation Processes
	S. A. Stern
Index	

Part l Electrically Driven Membrane Processes



Chapter I Basis of Electromembrane Processes

Robert E. Lacey*

Electrodialysis is the transport of ions through membranes as a result of an electrical driving force. It is the phenomenon underlying all electromembrane processes. If nonselective membranes that are permeable to ions (e.g., cellophane) are used in electrodialytic processes, electrolytes can be separated from nonelectrolytes. If the membranes are more permeable to cations than to anions or vice versa (e.g., ion-exchange membranes), the concentrations of ionic species in solutions can be increased or decreased by electrodialysis, so that practical concentration or depletion of electrolyte solutions is possible. With membranes of relatively recent origin that are more permeable to univalent ions than to multivalent ions, electrodialysis can be used to simultaneously separate and concentrate univalent ions from solutions containing mixtures of uni- and multivalent electrolytes.

This chapter presents a brief introduction to the basic principles common to all electrically driven membrane processes, a discussion of some of the variants of electrodialysis, and the future possibilities of membrane processes. These topics are discussed in detail later in this book and only briefly here.

I. HISTORICAL DEVELOPMENT OF ELECTRODIALYSIS

Although simple electrodialysis processes with nonselective membranes were studied in Germany during the early part of this century and the processes were reviewed and described in 1931 by Prausnitz and Reitstotter, it

^{*} Southern Research Institute, Birmingham, Alabama.

4 Basis of Electromembrane Processes

was not until 1939 that Manegold and Kalauch² pointed out the advantages of the use of highly selective membranes to achieve demineralization by electrodialysis. In 1940, Meyer and Strauss³ first proposed an electrodialysis process in which a number of anion-selective and cation-selective membranes were arranged between a pair of electrodes so that anion-selective membranes alternated with cation-selective membranes to form many parallel solution compartments, as illustrated in Figure 1. With such

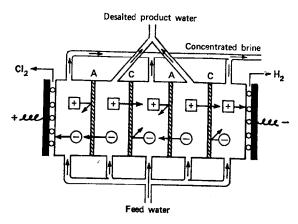


Figure 1: The electrodialysis process for desalination. A, anion-permeable membrane; C, cation-permeable membrane.

a multicompartment electrodialyzer, demineralization (or concentration) of solutions could be achieved (in a manner described later) in many compartments with only one pair of electrodes. With multicompartment electrodialysis, the irreversibilities represented by the decomposition potentials at the electrodes could be distributed over many demineralizing compartments and thus minimized, and the problems of handling the products formed at the electrodes could be minimized. With the development in the late 1940's of stable ion-exchange membranes of low electrical resistance, multicompartment electrodialysis became a practical process for demineralizing and concentrating solutions of electrolytes. During the 1950's the United States Department of the Interior's Office of Saline Water directly supported much research and development of the electrodialysis process for demineralizing saline water and encouraged research on the process by private companies. During the same span of years, the Netherlands National Research Organization, TNO, and the South African Council for Scientific

and Industrial Research developed the electrodialysis process for demineralizing saline waters originating in mines. In the years following 1955, the Office of European Economic Cooperation also supported research and development on the process, and in the 1960's the Institute for Arid Zone Research at Beersheva, Israel, made further contributions to the development of electrodialysis. In the late 1950's and the 1960's, several Japanese manufacturers developed the electrodialysis process as a means of concentrating seawater for use as a brine for the chlor-alkali industries.

A book on electrodialysis, edited by Wilson⁴ and published in 1960, describes the process primarily in terms of its use in saline water conversion. Chapters in books by Tuwiner⁵ and Spiegler⁶ also describe electrodialysis mainly as a desalination process. Reviews by Lakshiminarayaniah⁷ and by Friedlander and Rickles⁸ discuss the preparation of ion-selective membranes and the phenomena involved in membrane transport. Chapters in a book by Helferrich⁹ and in a privately published book¹⁰ treat in detail the physical chemistry of membrane transport.

II. ION-EXCHANGE MEMBRANES

Changes in the concentration of electrolytes in a solution can be accomplished by electrodialysis, if ion-exchange membranes are used. Ion-exchange membranes are ion exchangers in film form. There are two types: anion-exchange and cation-exchange membranes. Anion-exchange membranes contain cationic groups fixed to the resin matrix. The fixed cations are in electroneutrality with mobile anions in the interstices of the resin. When such a membrane is immersed in a solution of an electrolyte, the anions in solution can intrude into the resin matrix and replace the anions initially present, but the cations are prevented from entering the matrix by the repulsion of the cations affixed to the resin.

Cation-exchange membranes are similar. They contain fixed anionic groups that permit intrusion and exchange of cations from an external source, but exclude anions. This type of exclusion is usually called Donnan exclusion in honor of the pioneering work of F. G. Donnan. It is discussed in detail in Chapter 2.

The details of methods for making ion-exchange membranes have been reviewed recently. 4.7.8 In addition, reviews of methods of manufacturing ion-exchange membranes are included in the Annual Reviews of Ion Exchange Materials published by Industrial Engineering Chemistry magazine. Heterogeneous membranes have been made by incorporating ion-exchange particles into film-forming resins (a) by dry molding or calendering mixtures of the ion-exchange and film-forming materials; (b) by dispersing the ion-exchange

Table 1. Reported Properties of Ion-Exchange Membranes*

Manufacturer and Designation	Type of Membrane	Area Resistance (ohm-cm²)	Transference Number of Counterion ^a	Strength	Approximate Thickness (mils)	Dimensional Changes on Wetting and Drying (%)	Size Available
AMF ^b C-60 C-100	Cat-exch Cat-exch	(0.6 N KCI) 5 ± 2 7 ± 2	0.80 (0.5/1.0 N KCI) 0.90 (0.5/1.0 N KCI)	Mullen burst (psi) 45 60	12 8.5	10-13	44-in. wide rolls
A-60 A-100	An-exch An-exch	8 0 4 H 8 0	0.80 (0.5/1.0 N KCI) 0.90 (0.5/1.0 N KCI)	\$\$ \$\$	9	12-15	44-in. wide rolls
ACI° CK-1 DK-1	Cat-exch Cat-exch	(0.5 N NaCl) 1.4 1.8	0.85 (0.25/0.5 N NaCl) 0.85 (0.25/0.5 N NaCl)	Tensile strength (kg/mm²) 2 to 2.4		15-23	44 × 44 in.
CA-1 DA-1	An-exch An-exch	2.1 3.5	0.92 (0.25/0.5 N NaCl) 0.92 (0.25/0.5 N NaCl)	2 to 2.3	ه ه	12–18	44 × 44 in.
AGC ^d CMV CSV AMV ASV	Cat-exch Cat-exch An-exch An-exch	(0.5 N NaCl) 3 10 4 5	0.93 (0.5/1.0 N NaCl 0.92 (0.5/1.0 N NaCl) 0.95 (0.5/1.0 N NaCl) 0.95 (0.5/1.0 N NaCl)	Mullen burst (psi) ca 180 ca 180 ca 180 ca 150 ca 150	6 6 6	\$	44-in. wide rolls
IC ^f MC-3142 MC-3235 MC-3470	Cat-exch Cat-exch Cat-exch	(0.1 N NaCl) 12 18 35	0.94 (0./51.0 N NaCl) 0.95 (0./10.2 N NaCl) 0.98 (0./10.2 N NaCl)	Mullen burst (psi) ca 200 ca 165 ca 200	8 8	<38	40 × 120 in.

40 × 120 in.	18 × 40 in.	$40 \times 50 \text{ in.}$	Not given 40×50 in.
<39 Not given Not given	Cracks on drying	Not given	Not given
8 12 6 ⁹ 14	23	99	r r
ca 200 ca 165 ca 145 ca 200	Mullen burst (psi) 115 125 Mullen burst (psi)	ca 80	ca 150 ca 140
0.90 (0.5/1.0 N NaCl) 0.93 (0.5/1.0 N NaCl) 0.96 (0.1/0.2 N NaCl) 0.99 (0.5/1.0 N NaCl)	0.93 (0.1/0.2 N NaCl) ^b 0.93 (0.1/0.2 N NaCl) ^b (by electrophoretic	0.98 0.98	86.0 0.98
20 120 12 11	(0.1 N NaCl) 11 11 11	3	4 v
An-exch An-exch An-exch An-exch	Cat-exch An-exch	Cat-exch Cat-exch*	An-exch An-exch
MA-3148 MA-3236 IM-12 MA-3475R	II ⁱ CR-61 AR-111A	CL-2.5T CLS-25T	AV-4T AVS-4T

* Properties are those reported by manufacturer, except for those membranes designated with footnote g.

a Calculated from concentration potentials measured between solutions of the two normalities listed. American Machine and Foundry Co., Stamford, Connecticut.

^c Asahi Chemical Industry, Ltd., Tokyo, Japan.
^d Asahi Glass Co., Ltd., Tokyo, Japan.

Membranes that are selective for univalent (over multivalent) ions. Ionac Chemical Co., Birmingham, New Jersey.

Measured at Southern Research Institute.

Special anion-exchange membrane that is highly diffusive to acids.

Ionics, Inc., Cambridge, Massachusetts.

Tokuyama Soda Co., Ltd., Tokyo, Japan.

Univalent selective membranes.

8 Basis of Electromembrane Processes

material in a solution of the film-forming polymer, then casting films from the solution and evaporating the solvent; and (c) by dispersing the ion-exchange material in a partially polymerized film-forming polymer, casting films, and completing the polymerization.

Heterogeneous membranes with usefully low electrical resistances contain more than 65% by weight of the crosslinked ion-exchange particles. Since these ion-exchange particles swell when immersed in water, it has been difficult to achieve adequate mechanical strength and freedom from distortion combined with low electrical resistance.

To overcome these and other difficulties with heterogeneous membranes, homogeneous membranes were developed in which the ion-exchange component forms a continuous phase throughout the resin matrix. The general methods of preparing homogeneous membranes are as follows:

- Polymerization of mixtures of reactants (e.g., phenol, phenolsulfonic acid, and formaldehyde) that can undergo condensation polymerization.
 At least one of the reactants must contain a moiety that either is, or can be made, anionic or cationic.
- Polymerization of mixtures of reactants (e.g., styrene, vinylpyridine, and divinylbenzene) that can polymerize by additional polymerization. At least one of the reactants must contain an anionic or cationic moiety, or one that can be made so. Also, one of the reactants is usually a cross-linking agent to provide control of the solubility of the films in water.
- Introduction of anionic or cationic moieties into preformed films by techniques such as imbibing styrene into polyethylene films, polymerizing the imbibed monomer, and then sulfonating the styrene. A small amount of crosslinking agent (e.g., divinylbenzene) may be added to control leaching of the ion-exchange component. Other similar techniques, such as graft polymerization of imbibed monomers, have been used to attach ionized groups onto the molecular chains of preformed films.
- Casting films from a solution of a mixture of a linear film-forming polymer and a linear polyelectrolyte, and then evaporating the solvent.

Membranes made by any of the above methods may be cast or formed around scrims or other reinforcing materials to improve their strength and dimensional stability.

Table 1 shows the properties of some representative commercially available ion-exchange membranes as reported by the manufacturers.

III. CONCENTRATION AND DEPLETION BY ELECTRODIALYSIS WITH ION-EXCHANGE MEMBRANES

Figure 1 illustrates the principle of electrodialysis. An electrodialysis unit consists of a number of thin compartments through which solutions containing dissolved electrolytes are pumped. These compartments are separated by alternate cation- and anion-exchange membranes, which are spaced about 1 mm, or less, apart. The end compartments contain electrodes.

When electric current passes through the solution compartments and membranes, cations tend to migrate toward the negatively charged electrode (cathode) and anions tend to migrate toward the positively charged electrode (anode). The cations and anions in one set of solution compartments can pass freely through the cation- and anion-exchange membranes that are the walls of this first set of compartments. However, once the cations and anions are in the second set of solution compartments (the alternate compartments) cations are blocked from further transfer because the anion-exchange membranes will not allow their passage, and anions are blocked similarly from further transfer because they are blocked by cation-exchange membranes. An ion-depleted solution can be withdrawn from the first set of compartments; an ion-enriched solution can be withdrawn from the second set of compartments.

IV. CONCENTRATION POLARIZATION AND WATER-SPLITTING

The major limitation of the production rates achievable in electrodialysis units is concentration polarization at the surfaces of the ion-exchange membranes. Concentration polarization occurs because of differences in the transport numbers of ions in solutions and in the ion-exchange membranes. To illustrate the source of concentration polarization that occurs at an anion-exchange membrane, consider the fact that the transport number of anions in a solution is lower than it is in an anion-exchange membrane. Because of the lower transport number, the number of negative ions transported through the solution to the surface of an anion-exchange membrane by the electrical current is not sufficient to make up for the negative ions removed from that surface and transferred through the membrane. This deficiency of ions results in a reduction of the concentration of ions in the solution at the surface of the membrane. Eventually a concentration gradient is established in the solution such that the balance of the ions needed for steady-state

operation (i.e., those not supplied by the electical current) are supplied by the diffusional transport resulting from the concentration gradient.

At the other surface of an anion-exchange membrane accumulation of ions occurs because more ions are transferred through the membrane than can be carried away by the electric current (because the transport numbers are lower in solution than in the membrane). Thus, the concentration of ions in the solution at the surface of the membrane increases, and a concentration gradient is established in the solution that results in removal of the excess ions by diffusion.

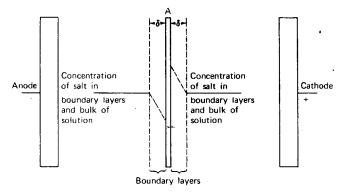


Figure 2. Concentration gradients that occur in boundary layers near membrane surfaces. A, anion-exchange membrane; δ , thickness of idealized boundary layer.

In Figure 2, concentration gradients of the types just described are depicted. In an electrodialysis compartment, the solutions flow past the membranes and a continuous velocity gradient extends from the surfaces of the membranes to the center of the flow channel. The flow channels are filled with spacer materials that cause complex flow patterns. The velocity of the solutions past the membranes and through the spacer materials results in relatively good mixing of the solution in the center portions of the flow channels, but the mixing is less near the surfaces of the membranes. Near the surfaces, boundary layers of almost static solution exist. In Figure 2, the so-called Nernst idealized model* of boundary layers has been depicted for simplicity in illustration.

^{*} In the Nernst idealized model of boundary layers, it is assumed that complete mixing of the solution in the center of the flow channels occurs, and that there is a sharp line of demarcation between completely mixed solution and the completely static solution in boundary layers adjacent to the membrane surfaces.

Concentration gradients as shown by the dashed lines in Figure 2 are established in the static boundary layers such that the concentration of ions at the solution-membrane interface on the side of the membrane that ions enter is lower than it is in the completely mixed zone. The concentration of ions at the interface on the other side of the membranes is higher than that in the completely mixed zone.

As the electric current density is increased these interfacial concentrations become lower (on the entering side) and higher (on the other side). As the current density is increased still more, the concentration of ions at the entering interface approaches zero. At this current density (termed the limiting current density) H⁺ and OH⁻ ions formed by ionization of water begin to be conducted through the solution and through the membrane. The OH- ions transferred through the membrane can cause deleterious changes of pH in the membrane and in the solutions in the boundary layers. Also, the layer of almost deionized water in the boundary layer on the entering side causes a large increase in resistance. Moreover, at current densities in excess of the limiting current density, little additional transfer of the desired ions is obtained because they are not available at the entering side. The increment of current above the limiting values results mostly in conduction of H+ and OH- ions from the so-called splitting of water, and in only a small amount of additional transport of the desired ions. Thus concentration polarization imposes a real limitation on the production rate (i.e., transport of desired ions) in an electrodialysis unit.

A detailed mathematical analysis of concentration polarization that relates the thickness of the boundary layers to the limiting current density is given in Chapter 2. The effects of velocity on the thickness of the boundary layers and on the limiting current density are also discussed in Chapter 2.

V. PROBLEMS AND LIMITATIONS OF CONVENTIONAL ELECTRO-DIALYSIS

Several problems have been encountered with the conventional electrodialysis process illustrated in Figure 1, in which both cation-exchange and anion-exchange membranes are used. Many of the problems are associated with the anion-selective membranes.

When the limiting current density is exceeded, the hydroxyl ions that are produced at anion-exchange membranes transfer through anion-exchange membranes and cause the concentrating solutions to become basic. If the concentrating solutions contain materials that form precipitates in basic solutions, such as Ca(HCO₃)₂, the concentrating compartments can become blocked by the precipitates and the electrodialyzers then become inoperative.

Such troubles with precipitating solids have been overcome in some instances by acidification of the concentrating solutions.

A more serious problem is encountered with the anion-exchange membranes that have been available up to 1970, when solutions containing large organic anions are treated. Organic anions driven into the matrix of the anion-exchange membranes by the electrical driving force become almost irreversibly attached to the surfaces of the positively charged anion-exchange membranes if the organic portion of the anion is large. Once this attachment occurs, the surface layer (i.e., the attached anion.) of what had been a positively charged anion-exchange membrane acquires a negative fixed charge and acts like a cation-exchange membrane. The result of these changes is that the resistance of the membranes increases and the selectivity decreases.

Because the operating lifetimes of anion-exchange membranes are often short when solutions with organic anions are treated, a variant of electrodialysis called transport depletion in which cation-exchange and neutral membranes are used has been developed to avoid the difficulties with fouling of anion-exchange membranes by organic materials.

Research is currently underway* to develop anion-exchange membranes with relatively porous matrices and with matrices based on aliphatic polymers instead of aromatic polymers. Either, or both, of these efforts may result in anion-exchange membranes that are less susceptible to organic fouling than the relatively tight, aromatic-based membranes in use now.

Although there are a few problems with conventional electrodialysis, such as those discussed above, there are only two serious limitations on the use of the process:

- The degree of concentration possible is limited by the water transferred through the membranes by osmosis and electroosmosis.
- The concentration of salts in the product water that is achievable with low energy costs is about 200-400 ppm of electrolytes because of the high cost of transferring ions through the high electrical resistances of solutions that are more dilute.

Despite these limitations electrodialysis, with its several variants, is a useful process for a number of industrial separations.

VI. VARIANTS OF ELECTRODIALYSIS

Several variants of the basic electrodialysis process have been developed to overcome some of the problems that have been encountered with the basic process.

^{*} Supported by the Office of Saline Water of the U.S. Department of the Interior.

A. Electrodialysis with Cation-Exchange and Neutral Membranes

In one of the variants of electrodialysis suggested by Deming and studied by Lacey¹¹ and by Lang and Huffman,¹² an array of alternate cation-exchange and nonselective neutral membranes is used, as shown in Figure 3. When

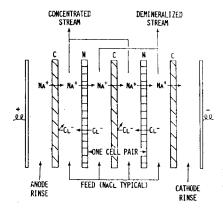


Figure 3. The cation-neutral transport depletion process. C, cation-selective membrane; N, neutral membrane.

direct electric current is passed through an assembly of this type, depleted and concentrated boundary layers form at the two sides of the cation-exchange membranes, but there is no such effect at the nonselective neutral membranes. The neutral membranes serve only to separate the depleted and concentrated boundary layers from each other and, in doing so, create alternate diluting and concentrating compartments.

The principal advantages of this electrodialysis process over the conventional electrodialysis process stem from the elimination of anion-exchange membranes and the attendant polarization and fouling problems. This process, therefore, permits greater flexibility in the selection of flow rates and current densities for a given application. The neutral membranes may also serve to screen solutes on the basis of molecular size and thereby contribute to a multiple-separation process. The use of this cation-neutral membrane process for demineralizing whey is discussed in Chapter 4.

B. Electrogravitational Demineralization and Concentrations

The electrogravitational process is an adaptation, in which ion-exchange membranes are used, of the much older process of electrodecantation discovered by Pauli¹³ in 1924 and applied commercially to rubber-latex separations by Stamberger¹⁴ in 1939. The term electrophoresis-convection was applied to this type of separation by Kirkwood¹⁵ in 1941. A comprehensive

treatise on electrophoresis was prepared by Bier. ¹⁶ The term electrogravitation appears to have been suggested by Murphy¹⁷ in 1950 because of the analogy with thermogravitation, and Frilette¹⁸ used the term electrogravitational transport when he reported on its applicability to demineralization in 1957. Kollsman¹⁹ has described some improvements on this technique and its application to other chemical separations.

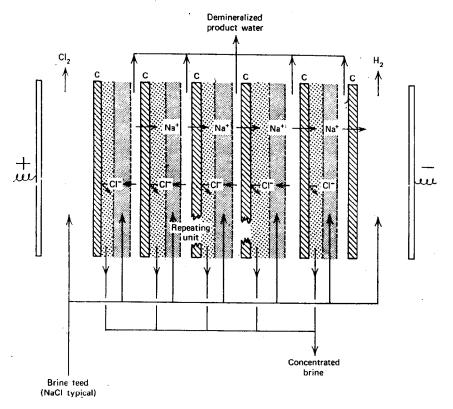


Figure 4. Electrogravitation with cation-selective membranes.

Electrogravitational demineralization may be achieved in a cell such as that depicted in Figure 4, in which only cation-exchange membranes are used. When a direct electric current is passed through a system of this type, depleted and concentrated boundary layers form at each side of the membrane just as they do in the previously described electrodialysis processes, but the solution in the depleted boundary layer rises and collects at the top of the

cell because it has a lower specific gravity than that of the bulk of the solution, and the solution in the concentrated boundary layer slides downward and collects at the bottom of the cell. During the continued passage of current, the density of the depleted layer is further reduced by electrical heating, which results from its relatively high electrical resistance. Conversely, the concentrated boundary layer has low electrical resistance and is subjected to the least electrical heating. Convective separation is thus augmented by the heating effects resulting from the passage of current. In operation, a depleted solution is withdrawn from the tops of the cells, and a concentrated solution is withdrawn from the bottoms of the cells, both at flow rates that do not disturb the convective flow within the cells.

One of the advantages of this process is the extreme simplicity of construction. The membranes may be placed loosely or simply hung in a tank fitted with electrodes, as shown by Murphy. The intermembrane compartments need not be isolated from each other with expensive frames or gaskets; imperfections in the membranes, even holes, will not seriously affect performance. The direction of electrical current may even be reversed without altering the locations at which depleted and concentrated solutions are removed. The pumping-energy requirements for this process are virtually nil because of the low flow rates usually employed, and maintenance of an electrogravitational cell is easy because of the simplicity.

Studies of the electrogravitational demineralization process by Mintz and Lang²¹ have shown that concentration gradients of greater than 100 to 1 can be achieved in cells only 6 in. high. Studies by Lang and Huffman¹² showed that electrogravitation is not competitive with other processes for demineralizing saline water but may be of interest for some industrial separations.

C. Electrosorption

In another variant of electrodialysis studied by Lacey and Lang^{22,23} under the sponsorship of the Office of Saline Water, three-layer membranes comprised of a neutral inner layer (which may be merely solution) sandwiched between a cation-exchange layer and an anion-exchange layer are used. Many of these three-layer membranes can be arranged between a pair of electrodes so that the solution to be treated flows between the membranes. No gaskets or solution manifolds are needed. The three-layer membranes are called electrosorption membranes. One method of forming them is to treat a flattened plastic tube (cellulosic dialysis tubing, for example) to impart anion-exchange properties to one face and cation-exchange properties to the other face. During the passage of a direct electric current, the solution on the outside of the electrosorption membranes is depleted and the solution within the