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2.500 Desalination and Water Purification
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Universität Stuttgart

ELECTROMEMBRANE PROCESSES: STATE-OF-THE-ART PROCESSES AND RECENT DEVELOPMENTS DEVELOPMENT

Summary

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ELECTROMEMBRANE PROCESSES, THEIR STATE OF DEVELOPMENT AND APPLICATION

Developed processes

electrodialysis → water desalination, salt concentration
diffusion dialysis → acid and base recovery from mixtures with salts
electrochemical synthesis → chlorine-alkaline electrolysis

Developing processes

bipolar membrane electrodialysis → production of acids and bases
continuous electrodeionization → regeneration of ion-exchange resins
energy conversion systems → low temperature fuel cells

To be developed processes

catalytic membrane reactors → hydrolysis of esters
electrodialysis hybrid processes → industrial waste water treatment

Never to be developed processes ?????

piezodialysis → water desalination
reversed electrodialysis → electrodialytic energy regeneration

ION-EXCHANGE MEMBRANES, THEIR FUNCTION AND PROPERTIES

Ion-exchange membranes are polymer films with fixed ions

anion-exchange membranes have positive fixed ions, e.g. $–NR_3^+$
cation-exchange membrane have negative fixed ions, e.g. $–SO_3^-$

required properties of ion-exchange membranes

- high ion selectivity
- low electrical resistance
- good form stability
- good chemical stability
- good temperature stability
- low cost

properties of state-of-the-art ion-exchange membranes* *

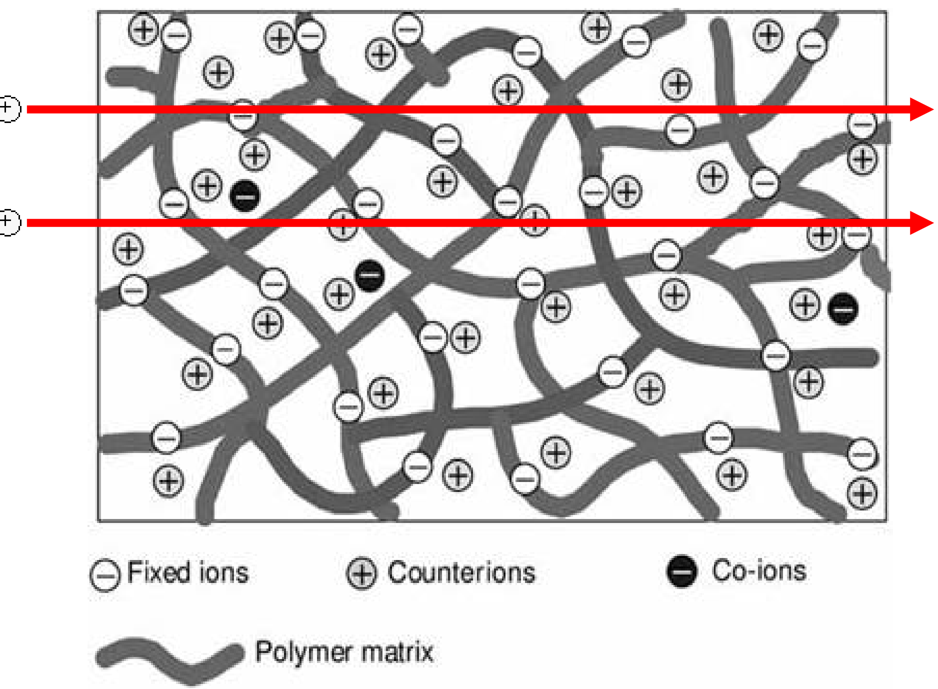
- ion selectivity 0.89 to 0.99
- area resistance 1 to 5 [Ω cm^2]
- swelling in solution 8 to 25Vol%
- stable in pH-range 1 to 14
- stable at a temperature < 130º C
- costs € 20.- to € 500.- per m^2

* properties determined in a 0.1 N NaCl solution

ION-EXCHANGE MEMBRANES AND THEIR STRUCTURES AND PROPERTIES

Homogeneous ion-exchange membrane

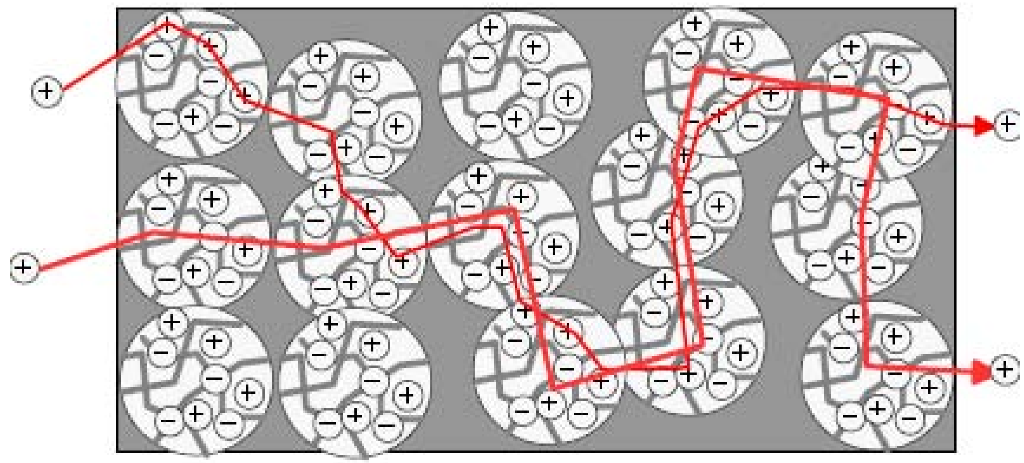
homogeneous polymer structure with fixed ions

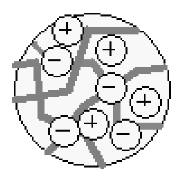


- high permselectivity and conductivity
- good mechanical properties
- high costs

Heterogeneous ion-exchange membrane

ion-exchange resin particles imbedded in a polymer film



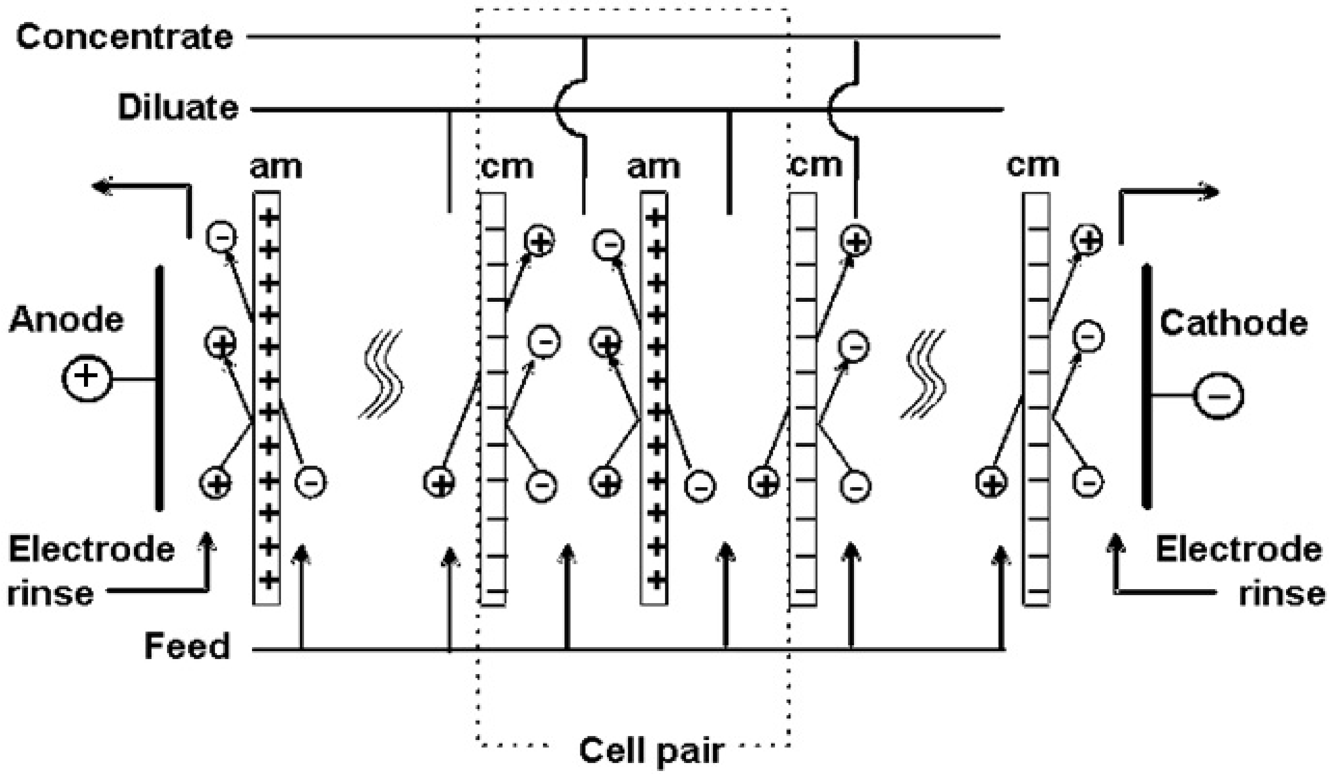


Ion-exchange resin particle
60 to 70 Vol% of membrane

- low permselectivity and conductivity
- poor mechanical properties
- low costs

CONVENTIONAL ELECTRODIALYSIS

The process principle

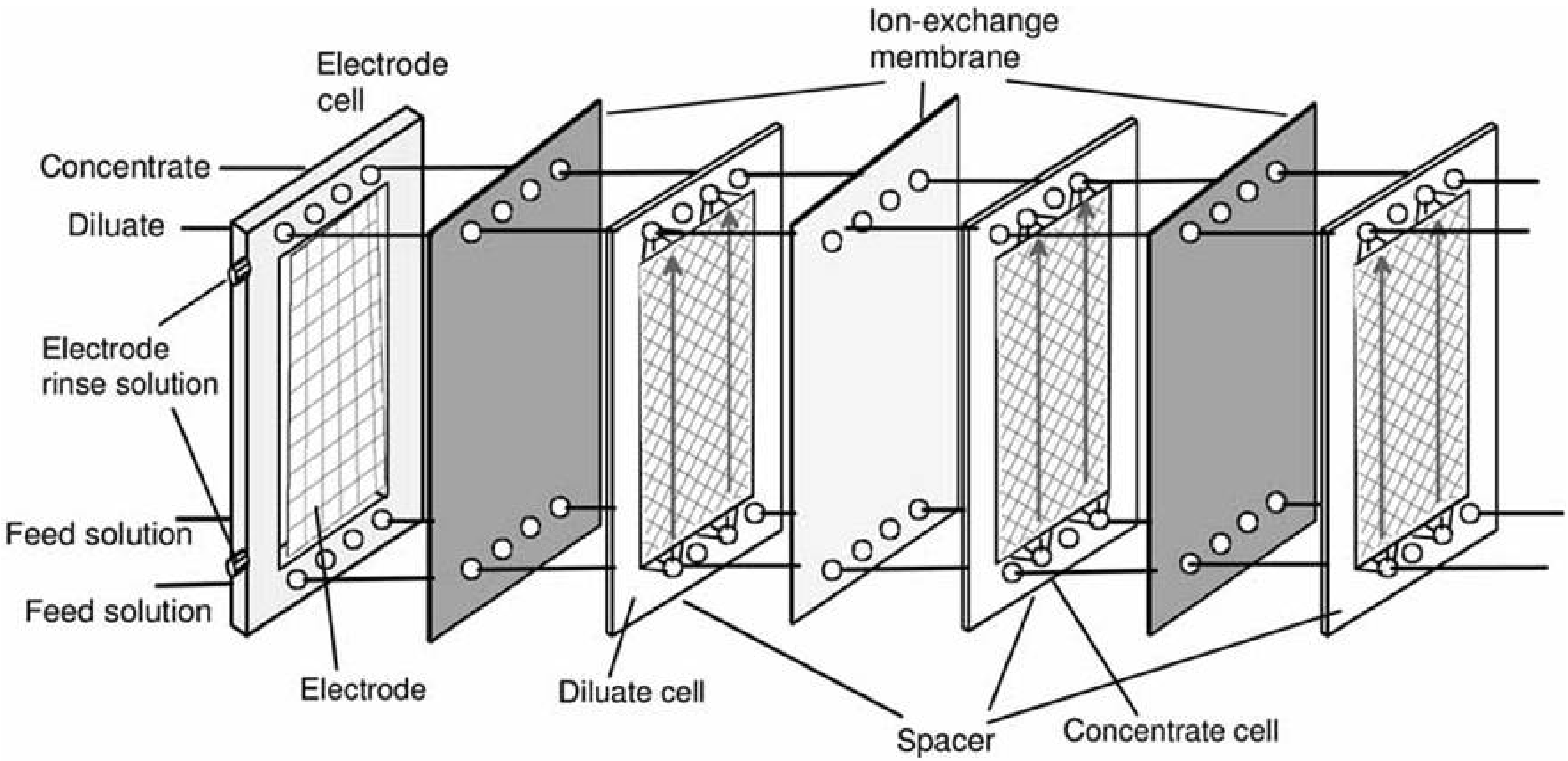


ions are removed from a feed solution and concentrated in alternating cells

a cation and an anion-exchange membrane, and a diluate and concentrate cell form a cell pair

CONVENTIONAL ELECTRODIALYSIS

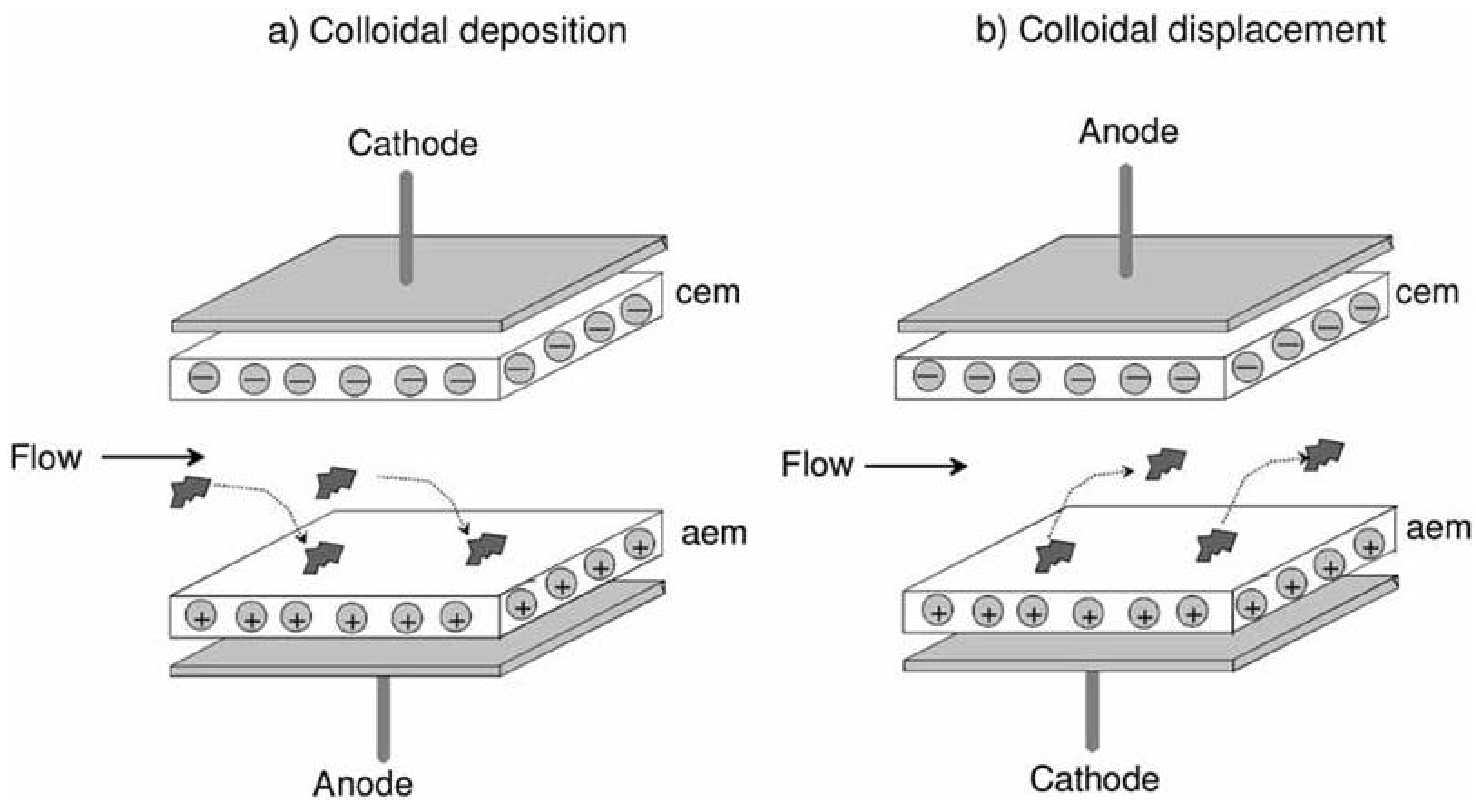
The electrodialysis stack



an electrodialysis stack is composed of 100 to 400 cell pairs between electrode compartments

CONVENTIONAL ELECTRODIALYSIS

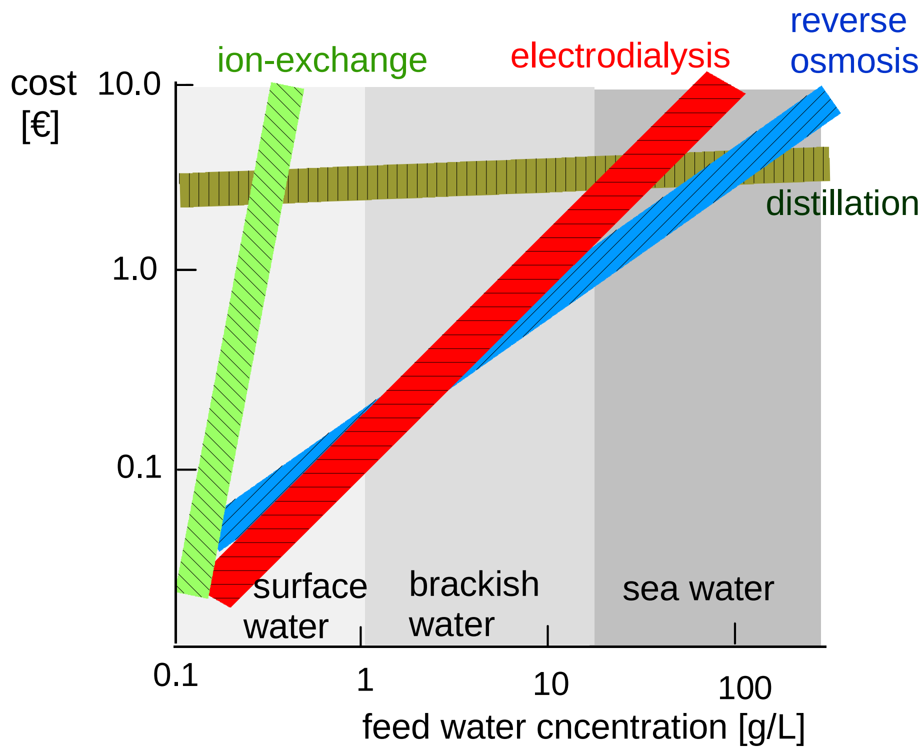
Reverse polarity operating mode



control of membrane fouling: “clean in place”

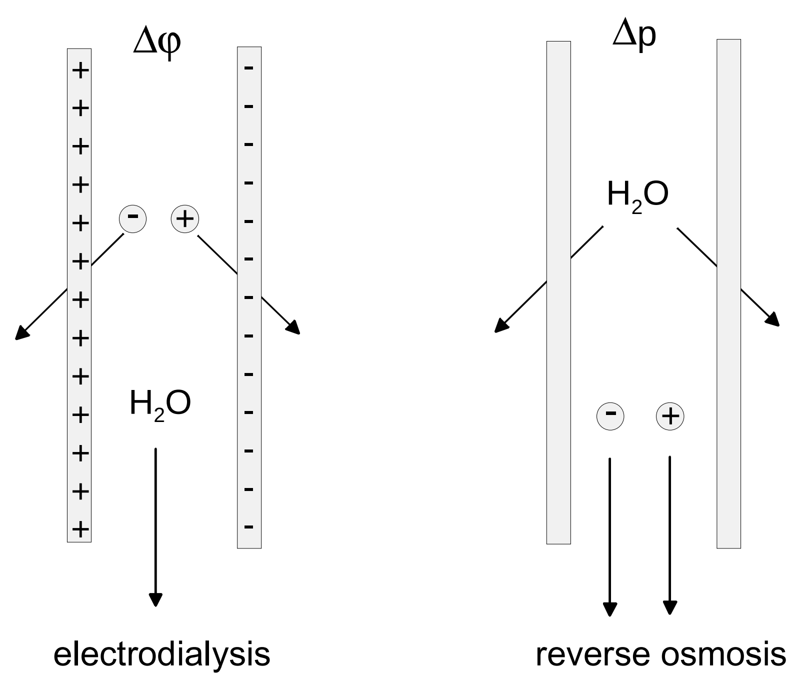
CONVENTIONAL ELECTRODIALYSIS

Water desalination costs



costs estimated for a required product concentration of < 0.2 g/L

Process principles of electrodialysis and reverse osmosis



irreversible energy loss proportional to ion transport ($E_{irr} = z_i$ F ΔC_i U V)

irreversible energy loss proportional to water transport ($E_{irr} = \Delta p\ V_{water}$)

CONVENTIONAL ELECTRODIALYSIS

Major applications

- brackish water desalination and waste water treatment
- sea water and brine concentration
- demineralization of food and pharmaceutical products

Advantages

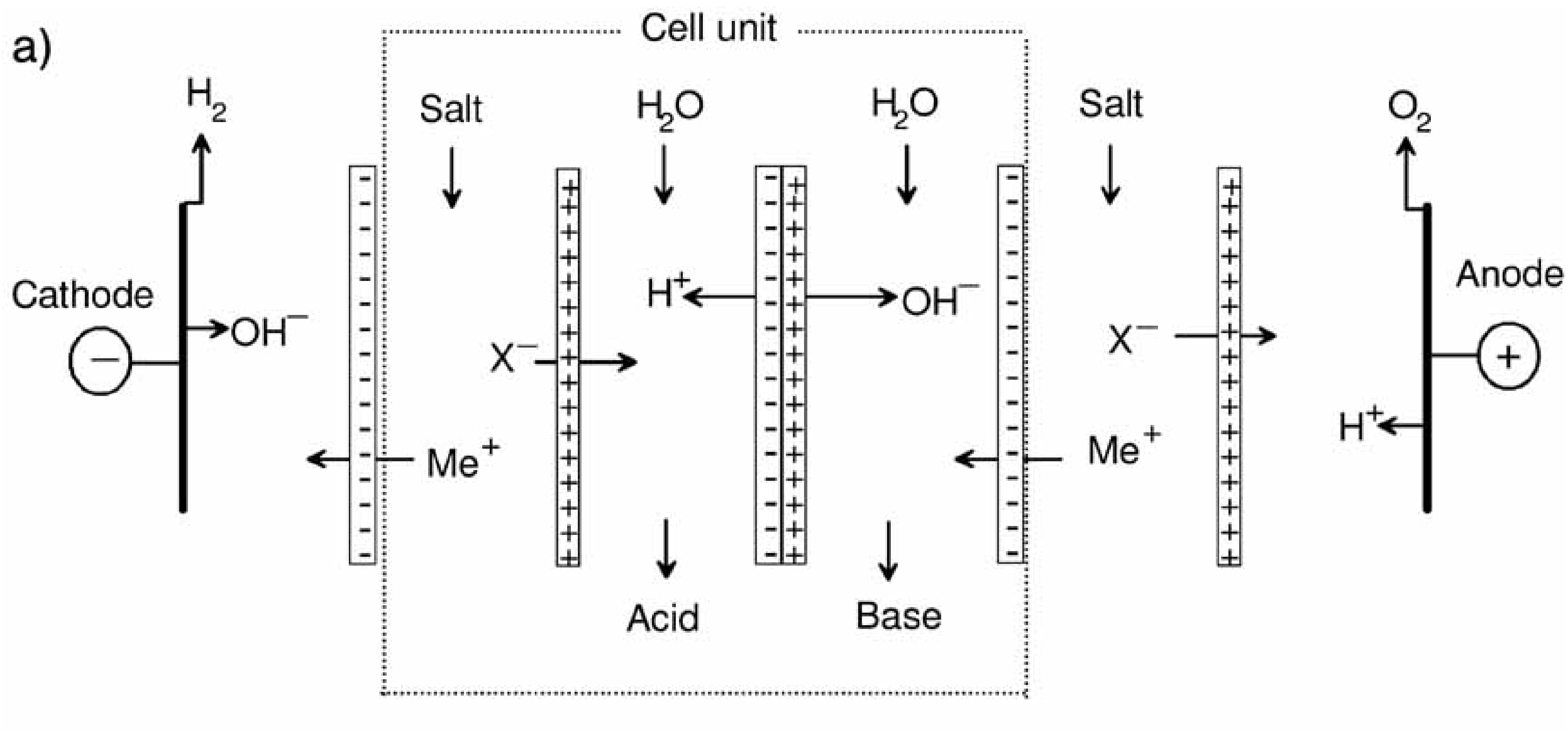
- high brine concentrations due to no osmotic pressure limitation
- low fouling and scaling due to reverse polarity operation
- good chemical and mechanical stability of membranes

Limitations

- only ions are removed from a feed solution
- low limiting current density at low diluate concentrations
- high energy consumption for desalination of concentrated feed solutions

ELECTRODIALYSIS WITH BIPOLAR MEMBRANES

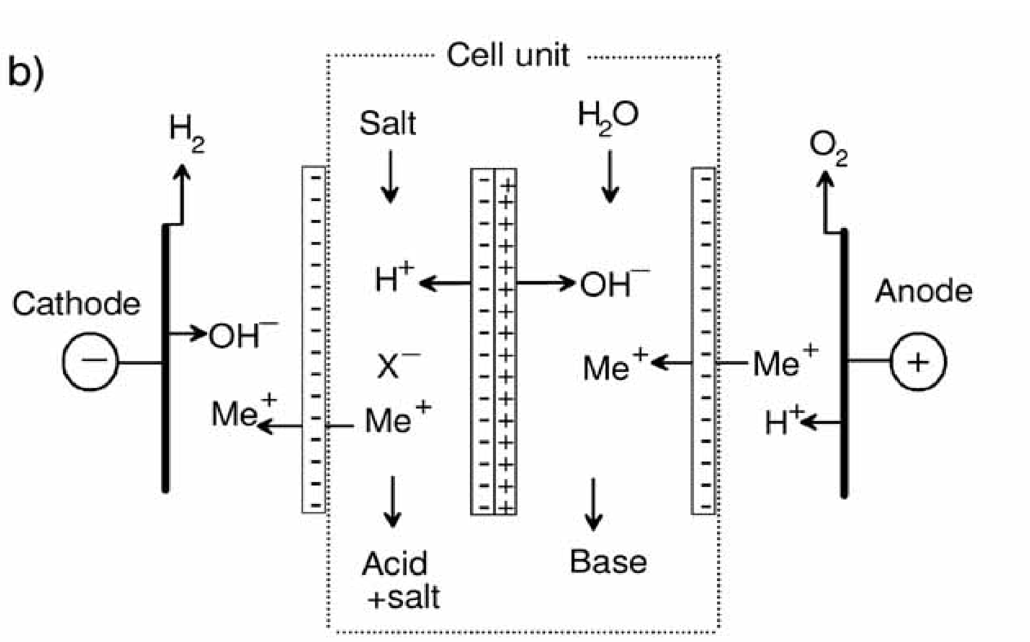
The process principle



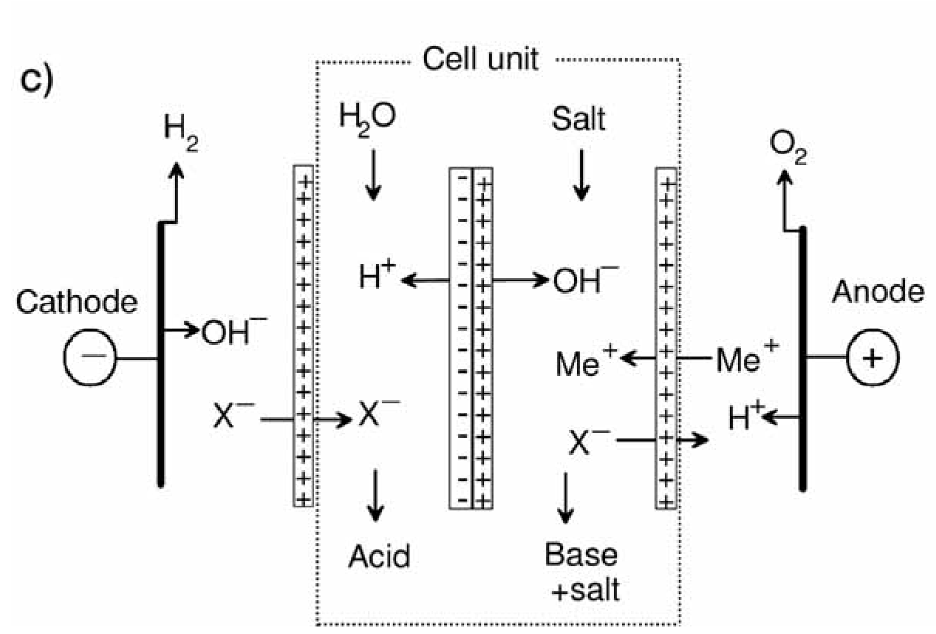
production of acids and bases from the corresponding salt solutions

ELECTRODIALYSIS WITH BIPOLAR MEMBRANES

The process principle



production of a pure acid and a base-salt mixture



production of a pure base and an acid-salt mixture

ELECTRODIALYSIS WITH BIPOLAR MEMBRANES

ICVT

Applications

- **recovery of organic acids from fermentation processes**
- **regeneration of ion-exchange resins**
- **recovering and recycling acids and bases from waste water**

Advantages

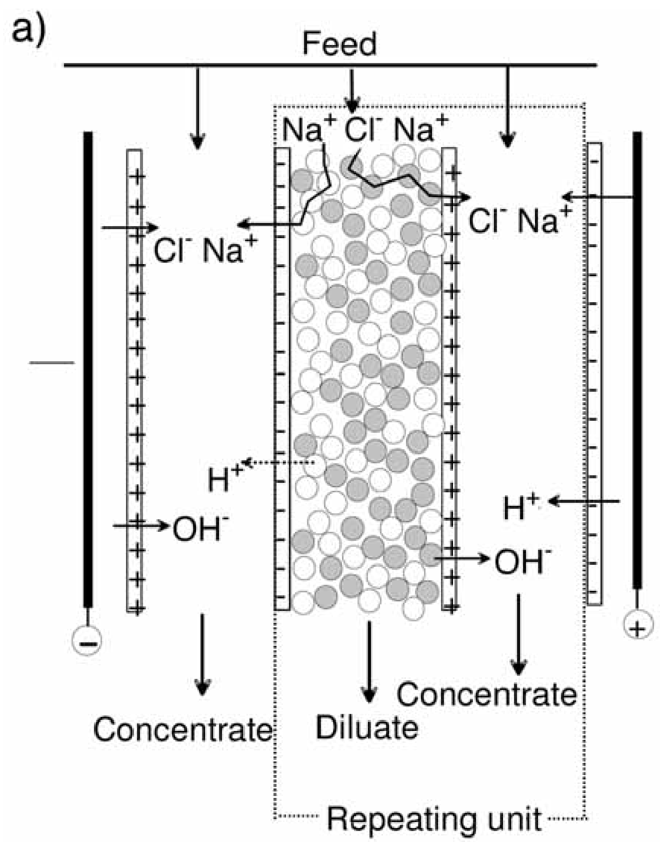
- **high energy efficiency**
- **relatively low initial investment costs**
- **no reaction by-products**

Limitations

- **contamination of product by salt due to incomplete co-ion rejection**
- **poor chemical stability of the membranes in concentrated acids and bases**
- **scaling due to precipitation of multi-valent ions at the membrane surface**

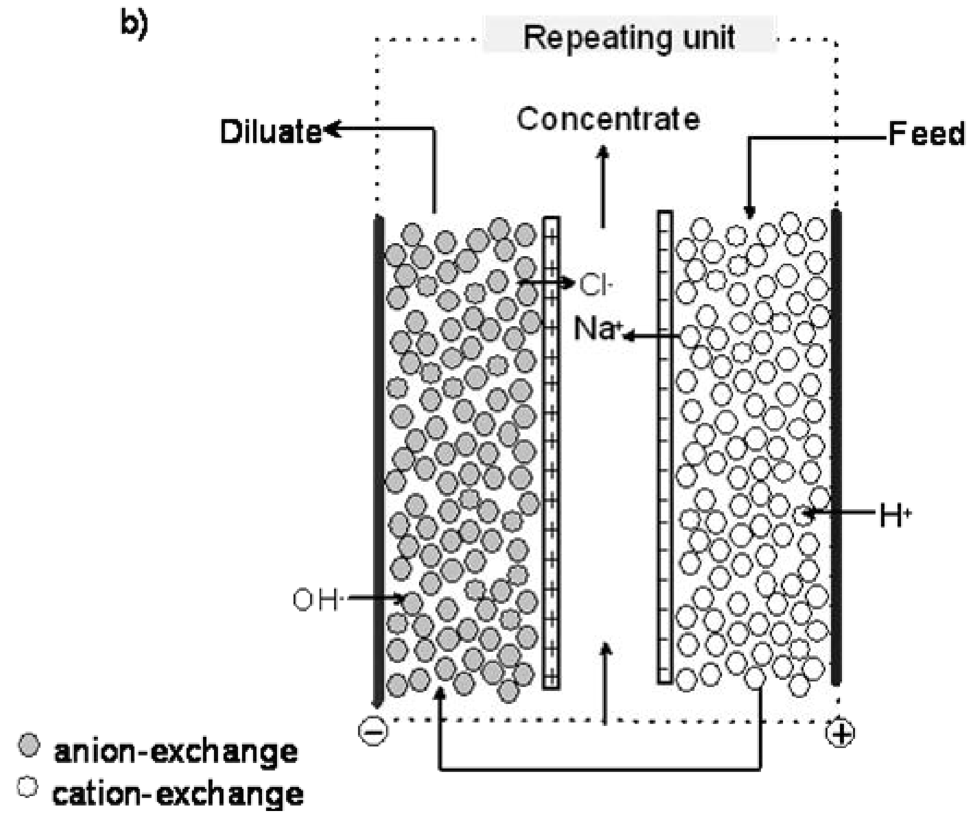
CONTINUOUS ELECTRODEIONIZATION

Mixed-bed ion-exchange resins



poor removal of weak acids
high electrical resistance
maximum achievable resistance < 12 M Ω cm

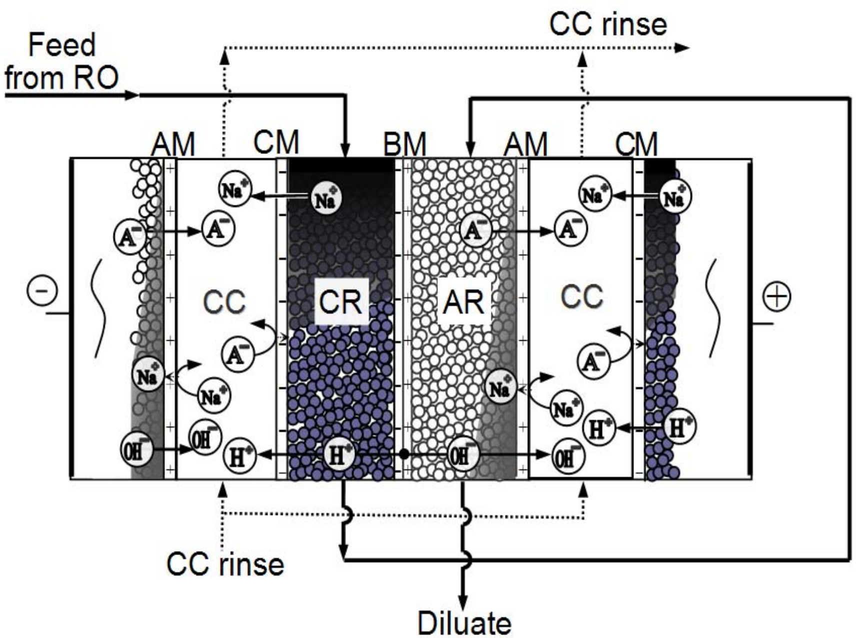
Cat- and anion-exchange resins in separate beds between electrodes



good removal of weak acids but electrode reaction by-products and cation leakage
maximum achievable resistance < 10 M Ω cm

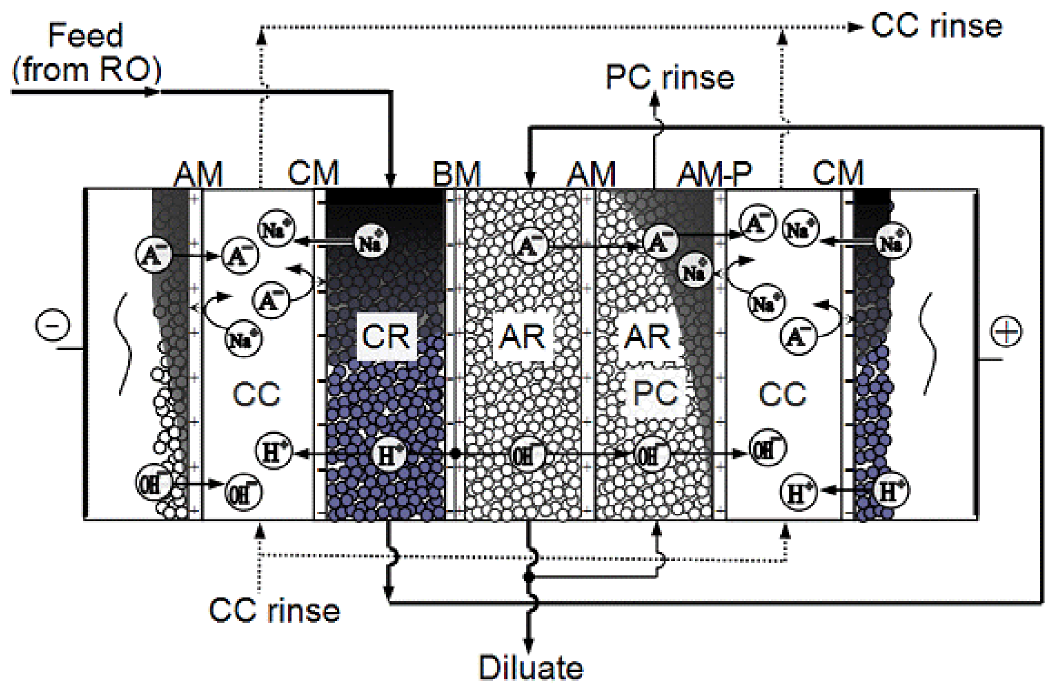
CONTINUOUS ELECTRODEIONIZATION

Separated ion-exchange resin beds and bipolar membranes



good removal of weak acids, repeating units can be stacked between electrodes, maximum achievable resistance < 10 M Ωcm

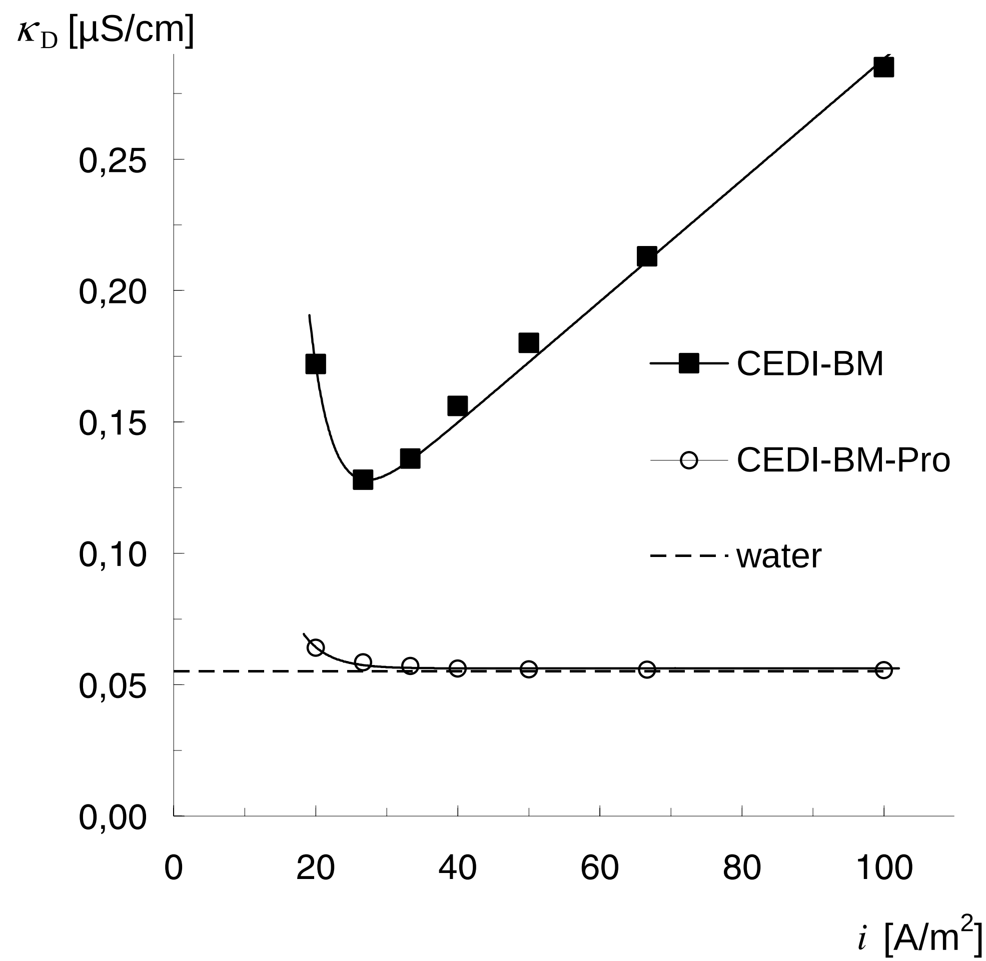
Separated ion-exchange resin beds, bipolar membranes and protection compartments



good removal of weak acids, repeating units can be stacked between electrodes, maximum achievable resistance ~ 18.0 M Ωcm

CONTINUOUS ELECTRODEIONIZATION

*Comparing CEDI with and without protection compartment **



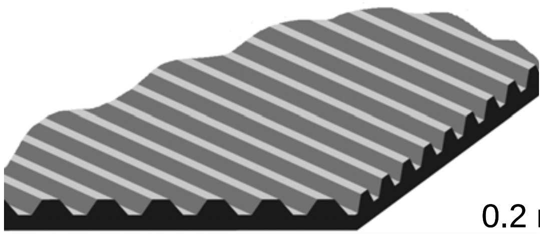
CEDI with protection compartment provides:

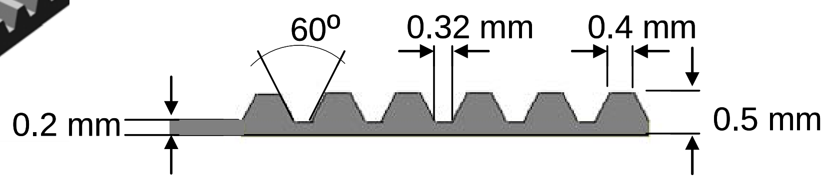
- **complete removal of weak dissociated acids and**
- **product water with a resistance of ~ 18.0 MΩ cm**

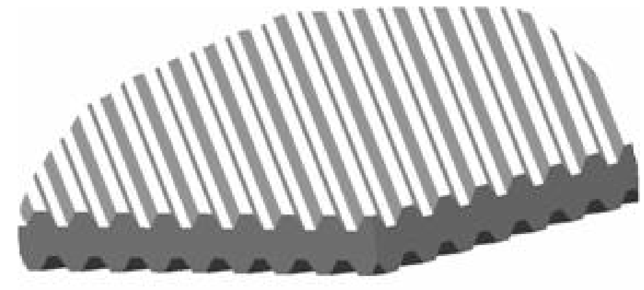
*reverse osmosis permeate is used as feed

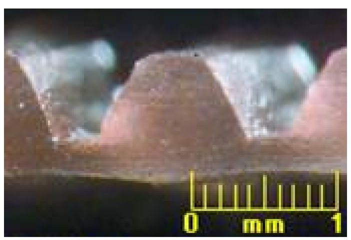
ION-EXCHANGE MEMBRANES WITH SPECIAL SURFACE STRUCTURES AND THEIR USE

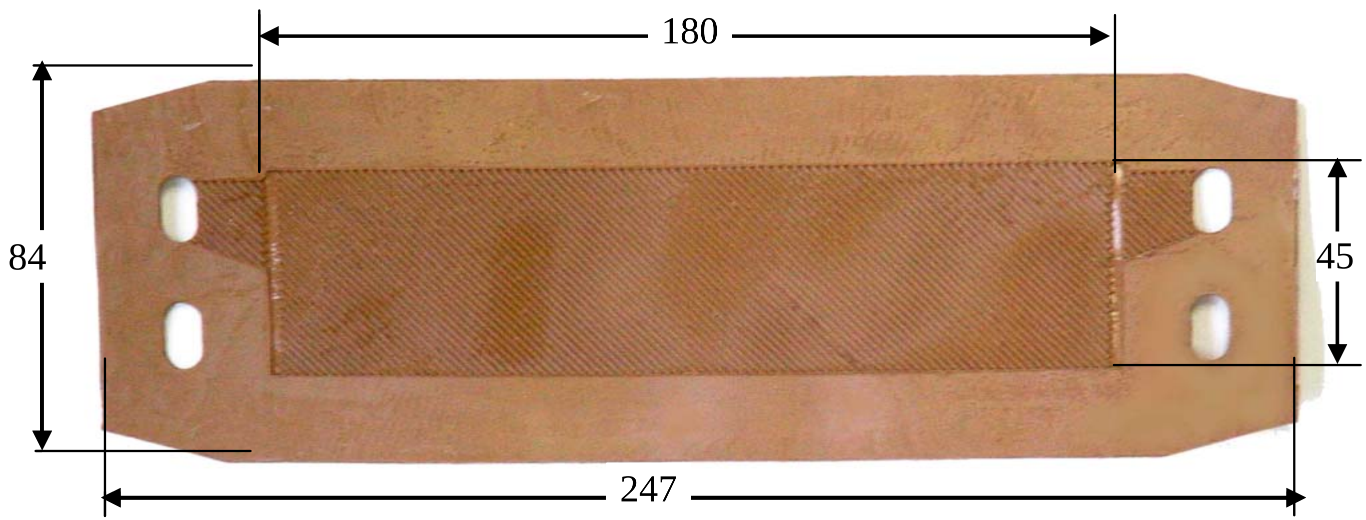
Preparation of surface modified membranes





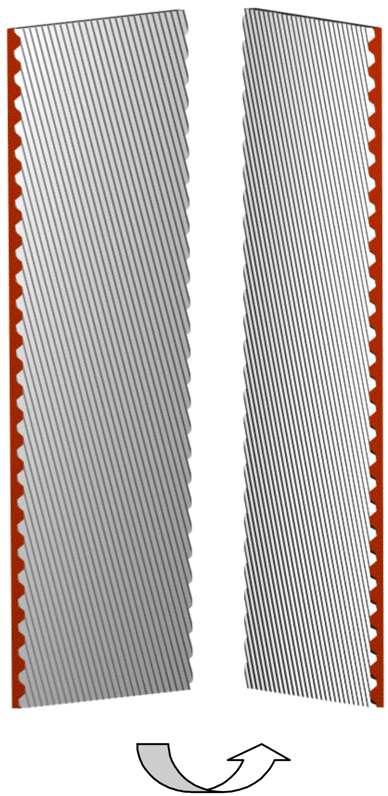


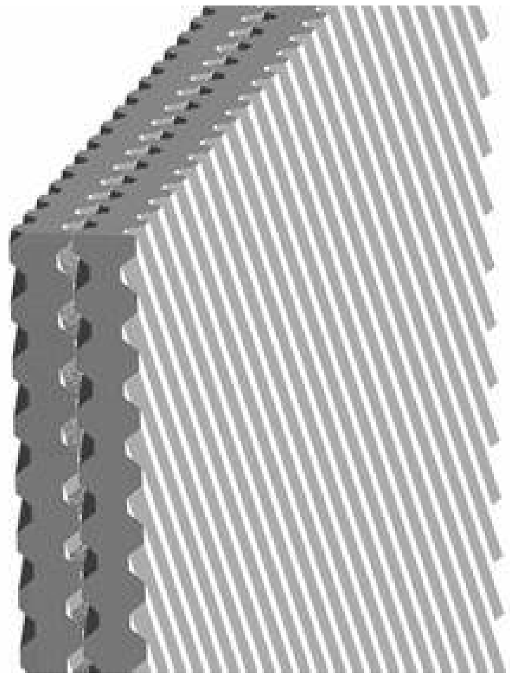


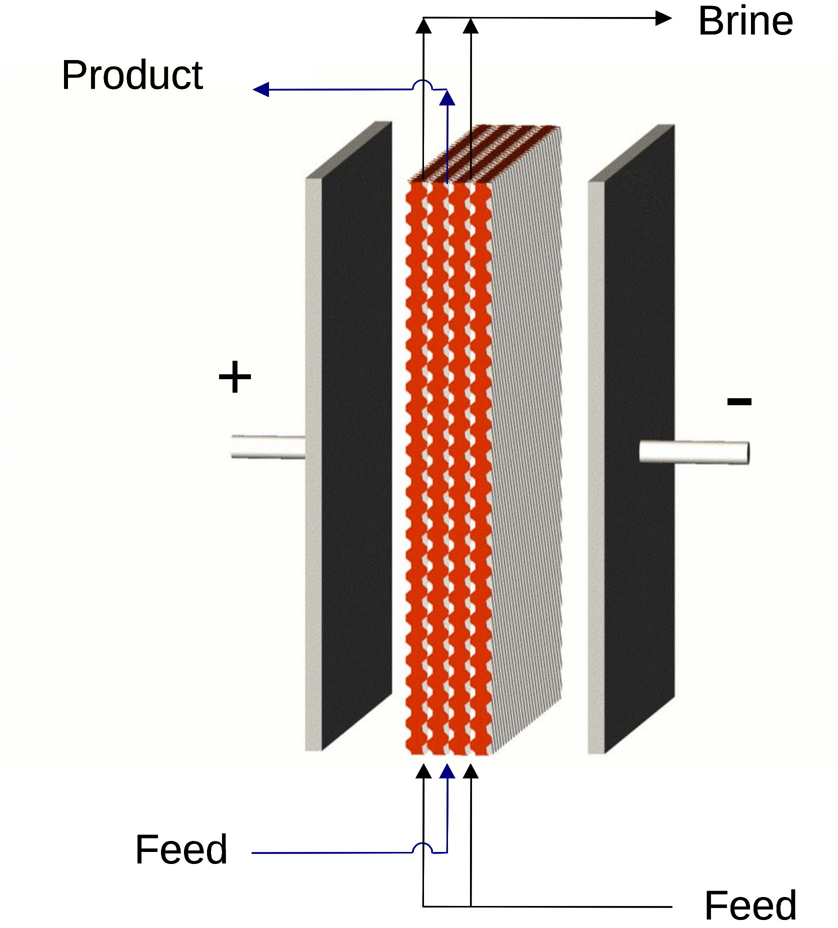


ION-EXCHANGE MEMBRANES WITH SPECIAL SURFACE STRUCTURES AND THEIR USE

The stack construction

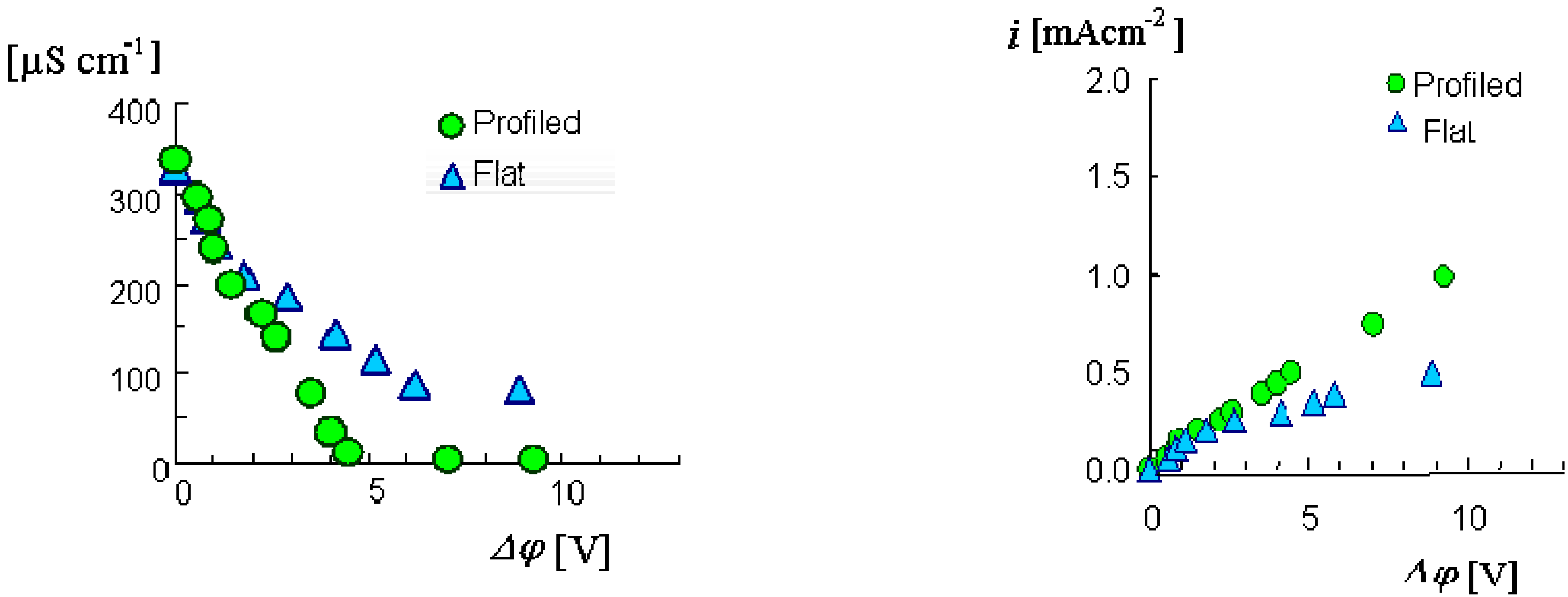






ION-EXCHANGE MEMBRANES WITH SPECIAL SURFACE STRUCTURES AND THEIR USE

Comparing performance of flat membranes and profiled membranes



current [mA m-2]	Δφ (cell) [V]	r (cell) [Ωm2]	κ(diluate) [µS cm-1]
0.28	5	1.6	100

current [mA cm-2]	Δφ (cell) [V]	r (cell) [Ωm2]	κ(diluate) [µS cm-1]
0.56	5	0.6	0.9

ION-EXCHANGE MEMBRANES WITH SPECIAL SURFACE STRUCTURES AND THEIR USE

Advantages

- high membrane surface area, i.e. less membrane area per unit plant capacity
- low achievable diluate conductivity, i.e. diluate conductivity ~1 µS/cm
- low cell resistance, i.e. low energy consumption
- contacts between the membranes, i.e. better pH-control
- no spacer needed, i.e. low investment costs

Disadvantages

- No long term practical experience

ELECTROMEMBRANE PROCESSES: EFFICIENT AND VERSATILE TOOLS IN A SUSTAINABLE INDUSTRIAL DEVELOPMENT

Conclusions

- Electrodialysis is a mature process used mainly for water desalination, brine concentration, demineralization of food products and treatment of industrial effluents
- Electrodialysis with bipolar membranes is an economic alternative for the production of acids and bases, however membrane properties are not satisfactory
- Continuous electrodeionization with bipolar membranes is an economic process for the regeneration of ion-exchange resins without any process by-products
- Donnan- and diffusion-dialysis serve presently only small market segments and piezodialysis and reverse electrodialysis are still highly uneconomical
- The use of electromembrane processes is changing from conventional electrodialysis to hybrid processes and catalytic reactors with specific industrial applications
- Membrane and membrane stack production costs must be reduced