New Anion Exchange Membranes for the Electrodialysis of Acids

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Aim of the work

- Minimization of proton leakage
- development of diffusion dialysis membranes
- evaluation of technical parameters for mineral acid production
- development and characterization of membranes for organic acids

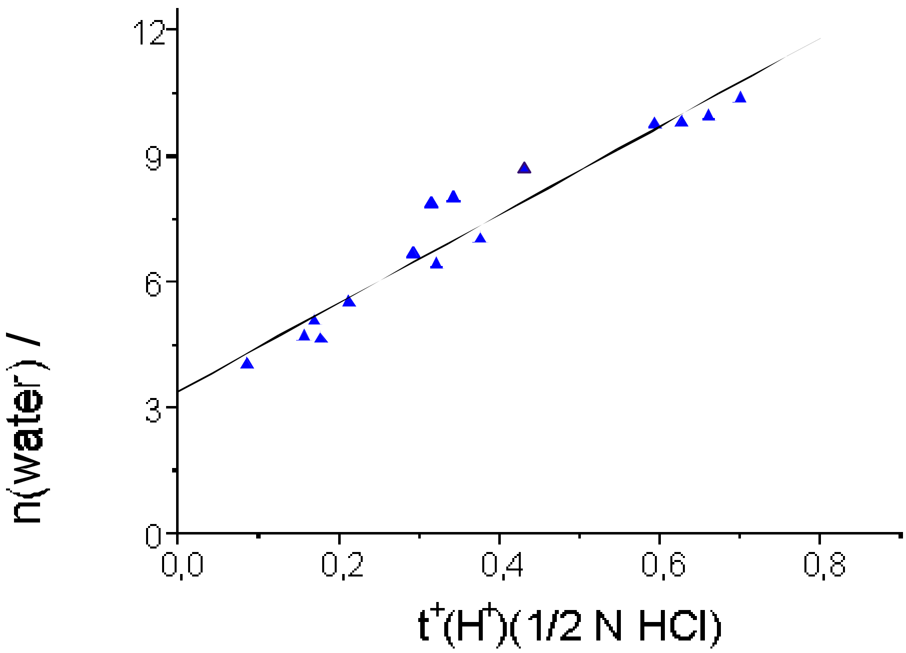
Proton leakage of anion exchange membranes

hydrochloric acid

Linear correlation between transference number of protons $t^+(H^+)$ and molar ratio of water per fixed ion (α factor).

sulfuric acid

Assumed additional formation of clusters. Ratio of membrane resistances in sulfate to chloride (β factor) sometimes abnormally high.



Influence of the water content per chloride on the transference number for protons $t^+(H^+)$. $t^+(H^+)$ measured at 25°C by potentiometric measurement between 1N and 2N

	Permselectivity in H_2SO_4	R (Na_2SO_4) / R(KCl) β - value
Acidblocker with cluster-effect	20	12
Acidblocker without cluster-effect	57	4

The ohmic resistance R of different membranes in 1 N KCl and 0,5 N Na_2SO_4 solutions (determined with Haber-Luggin electrodes [Lit 2]), their ratio (β value) and permselectivity P in sulfuric and hydrochloric acid.

Anion exchange membranes and organic acids

- Varied molecular mass (60 to 400 g mol^{-1}) of anions should be treated
- Too dense membranes result in fouling or high ohmic resistances
- Too open matrix structure result in high water transport [Lit. 3] and low current efficiency

Strategies for the preparation of optimized membranes are:

- Crosslinking: select the right pore distribution and size
- Selection of hydrophilic fixed ions to obtain high water content even at low ion exchange capacities
- Membranes for large anions (400 Dalton) have adapted ion exchange capacities

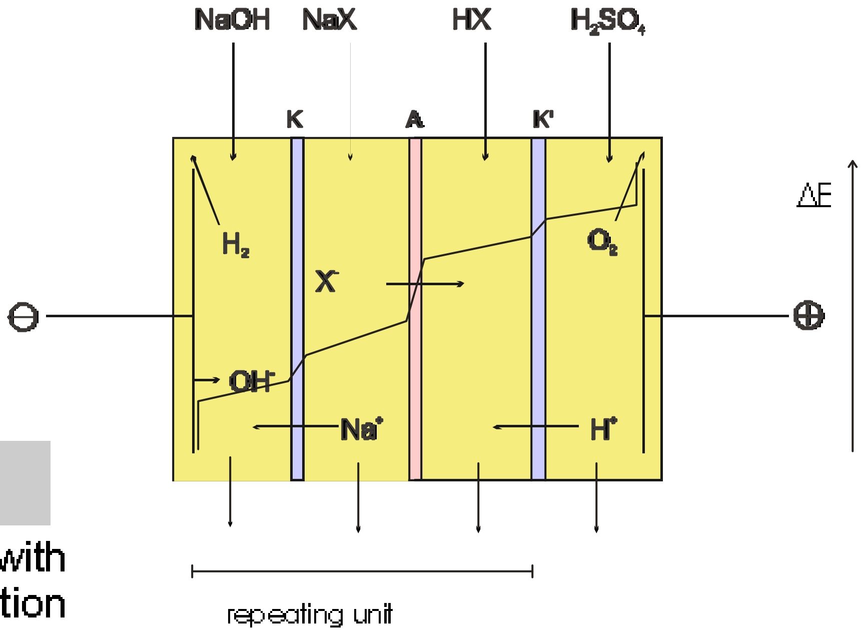
Optimized membrane series for electrodialysis

Membrane	optimized for	current efficiency*
PC Acid 35	hydrochloric acid	55
PC Acid 70	nitric acid	50
PC Acid 100	sulfuric acid	40
PC 100 D	acetic acid	91
PC 200 D	gluconic acid	94
PC 400 D	lactobionic acid	67
PC 35 DD	diffusion dialysis	-

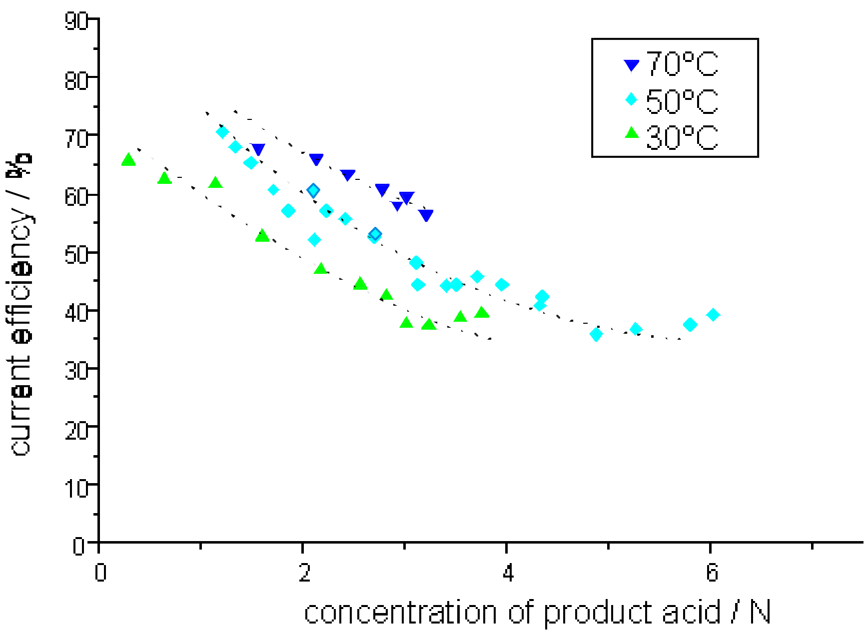
Use of optimized membranes in process technology

Test conditions

membrane area 320 cm^2
current density 1 kA m^2
K, K' cation exchange membrane
A anion exchange membrane



- current efficiency decreases with increasing product concentration
- elevated temperature improves the process remarkably
- current efficiencies of more than 50% for hydrochloric acid at room temperature possible
- current efficiencies of more than 50 % for sulfuric acid at elevated temperatures possible



Performance of membrane **PC Acid 100** at different temperatures. Experiments are conducted (see Fig.2) without the cation exchange membrane versus the anode chamber.

Temperature	energy consumption kWh $t_{(acid)}^{-1}$	current efficiency	byproducts NaOH / t	H_2 / Nm^3
30	6560	52	0,4	439
50	3000	65	0,4	351
70	2400	71	0,4	321

Production of organic acids

Acid	Membrane	energy consumption kWh t^{-1}	maximum concentration %
acetic	**PC 100D**	2000	24
citric	**PC 100D**	1950	33
gluconic	**PC 200D**	490	27
lactobionic	**PC 400D**	570	24

Splitting of sodium salts in the corresponding acids with optimized membranes. I = 1 kA m^{-2}; c_{Salz} = 0,5 N (lactobionic acid: 0,15 N)

The membrane **PC 35DD** is optimized in respect to high α values. According to the concentration high dialysis coefficients for acids are achieved.
Characteristic values are: U_{acid} = 9,1 mol hr^{-1} m^{-2} (mol l^{-1})

Results

An α factor is defined to predict proton leakage from membrane composition

A β factor is defined to select suitable membrane materials for multivalent mineral acid applications

energy consumption of salt splitting with presented membranes reach technically interesting regions

membranes suitable for production of large organic acids up to 400 Dalton from their salts are developed

Literature

[1]: a) T. Sata und Y. Yamamoto: Hydrophobic anion exchange membrane, Macromol. Chem., Rapid commun., 8 (1987), 611-614
b) R. Simons: Development of an acid impermeable anion exchange membrane, Desalination, 78 (1990), 297-302
c) I. Tugas, G. Pourcelly und C. Gavach: Electrodialysis of Hydrochloric Acid, J. Membr. Sci., 85 (1993), 183-194
[2] F. Helfferich: Ionenaustauscher, Verlag Chemie, Weinheim 1959
[3] S. Novalic, F. Jagschits, J. Okwor, K. D. Kulbe: Behaviour of citric acid during electrodialysis; Journal of Membrane Science 108(1995) 201-205