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Intensive current transfer in membrane systems: Modelling, mechanisms and application in electrodialysis

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A B S T R A C T

Usually in electrochemical systems, the direct current densities not exceeding the limiting current density are applied. However, the recent practice of electrodialysis evidences the interest of other current modes where either the imposed direct current is over the limiting one or a non-constant asymmetrical (such as pulsed) current is used. The paper is devoted to make the mechanisms of mass transfer under these current regimes more clear. The theoretical background for mathematical modelling of mass transfer at overlimiting currents is described. Four effects providing overlimiting current conductance are examined. Two of them are related to water splitting: the appearance of additional charge carriers (H^+ and OH^- ions) and exaltation effect. Two others are due to coupled convection partially destroying the diffusion boundary layer: gravitational convection and electroconvection. These effects result from formation of concentration gradients (known as concentration polarization) caused by the current flowing under conditions where ionic transport numbers are different in the membrane and solution. Similar effects take place not only in electrodialysis membrane systems, but in electrode ones, in electrophoresis and electrokinetic micro- and nanofluidic devices such as micropumps. The relation of these effects to the properties of the membrane surface (the chemical nature of the fixed groups, the degree of heterogeneity and hydrophobicity, and the geometrical shape of the surface) is analyzed. The interaction between the coupled effects is studied, and the conditions under which one or another effect becomes dominant are discussed. The application of intensive current modes in electrodialysis, the state-of-the-art and perspectives, are considered. It is shown that the intensive current modes are compatible with new trends in water treatment oriented towards Zero Liquid Discharge (ZLD) technologies. The main idea of these hybrid schemes including pressure- and electro-driven processes as well as conventional methods is to provide the precipitation of hardness salts before the membrane modules and that of well dissolved salts after.

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Abbreviations

CVC	current–voltage curve
DBL	diffusion boundary layer
EDL	electric double layer
LEN	local electroneutrality
NPP	Nernst–Planck and Poisson (equations)
pd	potential drop
QCD	Quasi-uniform Charge density Distribution
SCR	space charge region

Symbols

c_i	molar concentration of ion *i*
c_0 , c_{10}	molar electrolyte, counterion concentration in the solution bulk, respectively
c_{1s}^{I}, c_{1s}^{II}	counterion concentrations at the left-hand and right-hand membrane surfaces
c_{1m}	counterion concentration at the inner boundary of solution EDL
C_1	dimensionless counterion concentration normalized by c_{10}
d	thickness of the membrane
D	electrolyte diffusion coefficient
D_i	diffusion coefficient of ion *i*
E, $\tilde{E}$	electric field intensity, $\mathrm{V\,m^{-1}}$ and dimensionless, Eq. (22), respectively
F	Faraday constant
h	spacing between the membranes
i	current density
$i_{\lim}$	limiting current density
$I = 2i/i_{\lim}$	dimensionless current density, Eq. (22)
J_i	ionic flux density
k	chemical reaction rate constant
K	chemical reaction equilibrium constant
L_D	Debye length
Q	membrane ion-exchange capacity
R	universal gas constant
$Sc = \nu / D$	Schmidt number
t	time
t_i	transport number of ion *i*
T	absolute temperature
T_i	effective transport number of ion *i* in the membrane, Eq. (5)
$U = \lvert\Delta\varphi\rvert$	absolute value of pd, voltage
V	velocity, average velocity
x	normal to membrane coordinate in ED cell
X	dimensionless normal to membrane coordinate in ED cell, Eq. (22)
y	tangential coordinate in ED cell
z_i	charge number of ion *i*

Greek symbols

δ	Nernst's diffusion layer thickness
δ'	effective thickness of the DBL
δ_1, δ_2, δ_3	thicknesses of the different zones of DBL, Eq. (29)
$\tilde{\varepsilon}$	dimensionless small parameter in Poisson Eq. (9), defined by Eq. (15)
$\tilde{\mu}$	dimensionless small parameter in Eq. (16)
ν	solution viscosity
φ	electric potential
$\Delta\varphi_{Ohm}$	ohmic potential drop
Δc	concentration drop in the DBL expressed in $\mathrm{mmol\,cm^{-3}}$

Indices

i	ionic species
w	species produced by water splitting
1	counterion
Tilde	denotes dimensionless quantity

1. Introduction

Recent practice of electrodialysis has shown the interest of using intensive current regimes when the applied current exceeds its “limiting” value. Another even fresher discovery is the non-stationary currents, the pulsed and alternative ones, resulting in increased mass transfer in electrodialysis and in mitigated membrane fouling and scaling.

This review is intended to provide an insight into better understanding of the phenomena relevant to intensive current transfer through ion-exchange membranes (IEM) in electrodialysis (ED) and electrodeionization (EDI). The governing equations and boundary conditions used in the mathematical modelling of ion and volume electro-driven transfer are described; the main approaches to solving boundary-value problems are outlined. The mechanisms of overlimiting transfer are reviewed on the basis of mathematical description and using experimental data available in literature as well as our own results. The important role of the membrane surface is emphasized; some approaches to surface modification and the response in membrane macro-properties are considered. As for the applications of the knowledge about the intensive mass transfer, we have tried to describe the tendencies in ED/EDI practice, which follow from the possibility to realise higher rates of these processes.

2. Concentration polarisation

Let us consider a membrane system shown in Fig. 1a. An electrolyte solution flows between two plane ion-exchange membranes forming an electrodialysis cell. A direct current passes along the *x*-axis in the direction perpendicular to the membranes. Due to the difference of ion transport numbers in the solution and the