Electrochemical reactors

Reactor, where elect. energy <=> chem. energy conversion took place

- Material and shape of reactor
- Electrode shape and material
- Separators
- Mass transfer
- Potential distribution
- Electrolyzers connection

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Reactor shape and material

- Arrangement of reactor must reflect needs of desired application

industrial electrolysis – high currents, space utilization

growing / dissolving electrodes – continuous or frequent electrode treatment, accessibility

low concentrations – mass transfer, specific surface area,..

electroanalysis – low electrolyte volume

Basic parts of electrochem. reactor:

current connection
anode
electrolyte (+ separator)
cathode
current connection

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Current connection - supply

high values of direct current - high requests :

minimal resistance

short distance

good electric connection – contact resistance

also low resistance causes high losses

Problem: calculate power loss in Cu current connection of dimensions 2 x 20 cm, in the case of 10 kA distance 1 m.
$\rho(Cu) = 1,69\ 10^{-6}$ Ohm cm

$R = l \cdot \rho / A$ $\quad U=RI$ $\quad P=UI$

$R = 100 \cdot 1,69\ 10^{-6} / (2 \cdot 20) = 4,225\ 10^{-6}$ Ohm $\quad U = 4,225\ 10^{-6} \cdot 10^4 = 0,04225$ V

$P = 0,04225 \cdot 10^4 =$ **422,5 W**

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Electrodes

material: durability, overvoltage, electrolyte composition
shape: stirring, active surface

Shape and durability categories:

1. Dimension changing electrodes during process – dissolution or formation

2. Dimension stable electrodes (inert electrodes) – constant shape during process

Dimension changing electrodes

Growing electrodes
material deposition – galvanic metal deposition
production of MnO_2

$$\begin{array}{ll} \text{Anode:} & Mn^{2+} + 2\,H_2O \rightarrow MnO_2 + 4\,H^+ + 2\,e^- \\ \text{Cathode:} & 2\,H^+ + 2\,e^- \rightarrow H_2 \\ \hline \text{Overall:} & Mn^{2+} + 2\,H_2O \rightarrow MnO_2 + 2\,H^+ + H_2 \end{array}$$

Dissolving electrodes
anodic dissolution – metal rafination, electrochemical polishing/machining, electrocoagulation

lead accumulator

$$Pb_{(s)} + HSO_4^{-1} \Longleftrightarrow PbSO_4 + H^{+1} + 2e^{-1}$$
$$PbO_{2(s)} + HSO_4^{-1} + 3H^{+1} + 2e^{-1} \Longleftrightarrow PbSO_{4(s)} + 2\,H_2O$$

Inert electrodes

Application
gas evolution Cl_2, H_2, O_2,
oxidation/reduction org. comp.
production of ClO_3^-, ClO_4^-
fuel cells

Ideal inert electrodes
doesn’t exist (mechanical damage, corrosion, material fatigue, surface blocking,....) - usually described as dimension stable anodes (**DSA**)

Electrode material

Requests

high electronic conductivity, mechanical stability, easy formation to desired shape, valuable price, electrocalytic activity (overvoltage), inert in electrolyte

Durability

electrode replacement – process shut down – economic losses

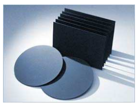
desired longest operation period

Inert electrode materials

Cathode: reduction conditions – wide range of materials most metals (Pt, Ir Pd, Ni, Fe, SS, Hg). Non metallic materials – graphite, carbides, borides, diamond electrodes, ceramics

Anode: oxidative environment – limiting for most metals - Pt metals. Non metallic materials – graphite, diamond electrodes. Most common - ATA electrodes (Ti + oxides Ir or Ru)

ATA electrode



diamond electrodes

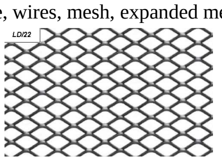
Electrode shape

Requests

easy replacement, connection to current, gas removal, minimal interelectrode distance, mass transfer,

Frequently

plate, cylinder, tube, wires, mesh, expanded metal



Mass transfer limitation

- heterogeneous process

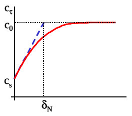
Electrode reaction take place on electrode – solution interface.

Important factor - Mass transport of reactant to the electrode surface
- problem in diluted solutions

- Nernst - Planck equation of mass transfer

$$\vec{J}_i = -D_i \nabla c_i - z_i u_i c_i \nabla \varphi + \vec{v} c_i$$

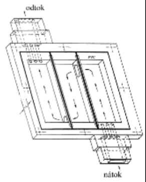
- difusion
- migration
- convection



Immobile film model

concentration gradient at electrode surface

Mass transfer



calculation of process intensity – film model

$$J = D\frac{c_0 - c_s}{\delta_N} = k\left(c_0 - c_s\right) \qquad j = nFJ$$

possible enhancemnet:

- increase of c_0
  - more concentrated solutions
- intensive hydrodynamics e.g. mixing (δ_N)
  - local overall
  - energetic and material issues
- increase of electrode surface
  - specific performance
  - accessible materials

Calculation of mass transfer coefficient

simple rectangular channel (desk elyzer) n = 8 c^0 = 1g dm^{-3}

$$Sh = \frac{kd_e}{D} \qquad Re = \frac{d_e v}{\nu} \qquad Sc = \frac{\nu}{D}$$

I. Roušar, J. Hostomský, V. Cezner and B. Štverák *J. Electrochem. Soc.* **118** (1971) 881

$$Sh = 1.85\left(\frac{d_e}{l} \cdot Re\, Sc\right)^{1/3}$$

k = 3.4·10^{-6} m s^{-1}

j_{lim} = 42 A m^{-2}

Mass transfer as limiting factor

- commercial arrangement in reactors

electrode	flow velocity [m s^{-1}]	k [m s^{-1}]	c_{min} [mol m^{-3}]
desc electrode	1	$1x10^{-5}$	5
rotating cylindrical electrode	10	$1x10^{-4}$	$5x10^{-1}$
porous electrode (RVC)	0,10	$1x10^{-2}$	$5x10^{-3}$
3D electrode (particles)			
packed bed	0,10	$2x10^{-4}$	$5x10^{-4}$
fluidised bed	0,01	$6x10^{-3}$	$1x10^{-2}$

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zdroj: L.J.J. Janssen, L. Koene, *Chem. Eng. J.* **85** (2002) 137

Separators

Separators divide cathodic and anodic chamber, protection towards electrolytes and reaction products (gases) mixing

Diaphragm – inert non-conductive porous barrier (azbestos, PVC, PE, PTFE,...) only limited separation

Membrane – ion selective barrier permeable only for charged ions of one polarity

Nafion[R]

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Ion exchange membranes

ion exchange (ion selective) membrane - foil or sheet prepared from ion exchanger

main task isn't ion exchange but selective transport across

charge of active groups in membrane is compensated by ions with opposite charge - counterions

occurrence of membrane defects causes penetration of ions charged as active groups fixed in membrane

similarly to ion exchangers:

Cation selective - enables transport of positive charged ions

Anion selective - enables transport of positive charged ions

bipolar - (special kind) membrane consisting from cation and anion selective layers

Electrolyte

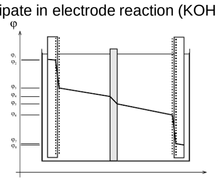
Ion conductive media – 2nd order electric conductor – higher temperature leads to higher conductivity

Solution – dissociated ions in solvent (water)

Molten salt – ions mixture

Highest conductivity – minimal ohmic losses.

Supporting electrolyte – ions increasing electrolyte conductivity but don't participate in electrode reaction (KOH in alkaline water elz.)



potential profile in electrolyser

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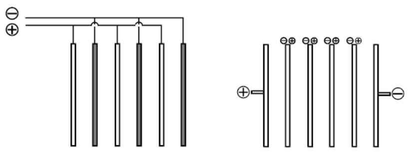
Electrode connection

Industrial electrolysers are equipped with many electrodes following size and performance of electrolyser.

Arrangement

monopolar - each electrode connected individually

bipolar - only side electrodes are connected



monopolar and bipolar arrangement

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Power source

Problem: Calculate power source parameters for electrolyser consisting 20 electrodes for H_2 production of 50 dm^3 /hod (101 kPa, 20°C) in the case of monopolar and bipolar arrangement. Voltage of each anode/cathode pair is 1,8V. Neglect current loss in conductors, transformation etc. .

$n_{H2}=V/Vm$ Vm=24dm^3/mol n_{H2}= 2.083 mol/hod

$Q = n_{H2} \cdot z \cdot F$ I=Q/t I=2.083 2 96500/3600= 111.7 A

a) monopolar

power source U =1,8V I=111,7 A P= 201,4 W

b) bipolar

power sourc. $U=19 \cdot U_{cell}$=34,2 V I= 111,7/19= 5,88 A P= 201,4 W

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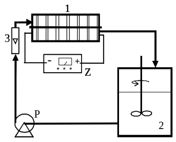
Reactor operation mode

Batch – closed cycle till desired product concentration

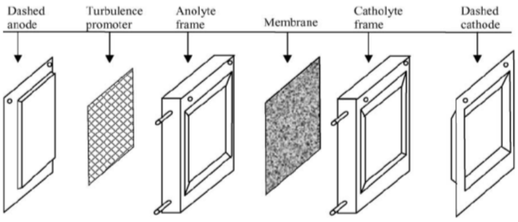
One pass – all conversion occurs during one flow through reactor

Feed and bleed - combination of previous. Fresh solution supplied to the reservoir and depleted solution is removed from reservoir in one moment



batch mode

Filter-press electrolyzer



Most frequent cell construction

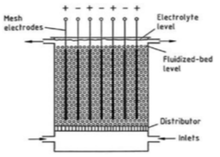
Suitable for processes with “high” electroactive compound concentration
Anodic and cathodic chambers separated by membrane or diaphragm

Cell with fluidized bed of inert particles

- advantages
  - mass transfer enhancement
  - mechanical electrode surface treatment
  - advantages of 2D electrodes

increase of k (mass transfer coeff.) by one order - 10 times lower outflow concentrations

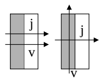
- application
  - cathodic metal electrowinning
  - diluted solutions with electrode surface inhibition



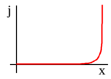
Chemelec^R BEWT

3D electrodes

- construction arrangement
  - "flow-through"
  - "flow-by"
  - fluidized bed

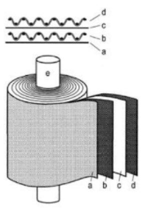


- disadvantages
  - complicated process control
  - discontinuous process
  - electrode price (some cases)

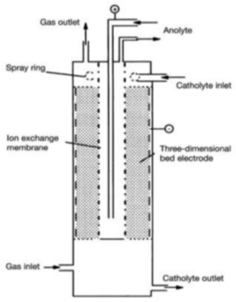


- advantages
  - high specific surface
  - high mass transfer
  - high specific yield
  - treatment of very diluted solutions

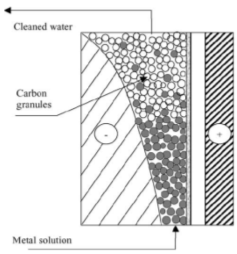
3D electrodes - static



Swiss roll cell
a- Ni anode
c – SS cathode
b d - PE separator
e – current feeder



enViro cell



Application	Metal	Throughput, m^3/h	Concentration, ppm Inlet	Concentration, ppm Outlet
Production of measuring instruments	Hg	0.3	300	0.05
Film processing	Ag	0.2	15	1.0
Salt production	Pb	0.5	2	0.1
Electroplating	Cd	0.2	20	1.0
Battery production	Hg/Cd	0.08	500	0.01
Cellulose acetate production	Cu	20	20	1.9
Pickling (recycling of solution)	Cu	3	150	50
Dye production	Cu	6	400	2.0
Dye production	Hg	2	4	0.05

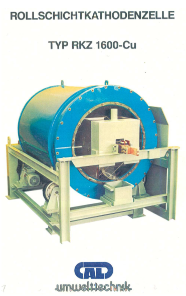
3D electrodes - moving

- static 3D electrodes – potential risk of pore blocking by electrodeposited metal or by mechanical impurities

  solution – moving 3D electrodes

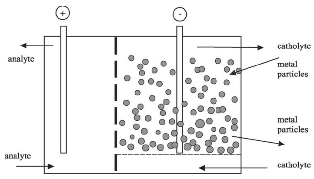
- arrangement
  - moving particle bed
  - pulsating particle bed
  - fluidizing bed

- still discontinuous process

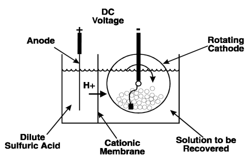


3D electrodes - moving

Rota-Cat^{TM}, *Trionetics, Inc.*

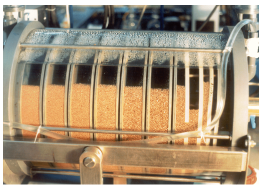


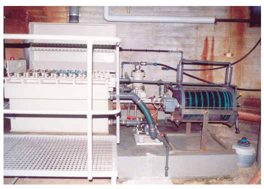
fluidizing bed – charge transferred by particle touching

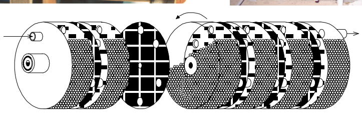


moving particle bed – cathode particles still in contact

3D electrodes – moving with self-ordering effect (VMPB)







rotating cascade of 3D particle bed cathodes with self-ordered particle distribution for continuous galvanic rinse water treatment

Reactor design

- known principles from scale up from small size
- Matematical modeling
  - increasing performance of compoters enable more and more sophisticated models
  - enable internal phenomenon description and design optimisation