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Electrochemical Engineering

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Mass Transfer by Fluid Flow, Convective Diffusion and Ionic Electricity Transport in Electrolytes and Cells

5.1 Introduction

The performance of electrochemical processes is not only determined by charge transfer and electrode kinetics, but a number of additional phenomena cause and rule the electrode kinetics (in the microkinetic as well as macrokinetic sense), the heat balance of the cell and the mass balances of all process streams (electrolyte, gases, solid products). Among these factors the fluid dynamic conditions, under which the electrolyte enters, passes and leaves the electrolysis cell or moves in it under free convection, is the most powerful process parameter since hydrodynamics rule mass and heat transport.

Heat transport is important as it controls together with heat generation the temperature distribution in the cell. Another condition typical for electrochemical processes is charge transport through the electrolyte, which together with electrode kinetics determines in particular the current density distribution across the electrode surface. It may determine the overall current efficiency, conversion selectivity and space time yield of the process by local inhomogeneities of the current density for instance by locally too high current density which might exceed the mass transfer limited current density.

The proper handling of these characteristic process determinants: fluid dynamics, mass transport and heat transport together with proper management of ionic charge transport are the main subjects of electrochemical process engineering as far as the reactor i.e. the electrolyzer is concerned. But the electrochemical engineer has to be aware that the cell alone is only one part of the whole process. Electrolyte make up, product isolation and recycling of the electrolyte have to be taken into consideration, too.

5.2 Fluid Dynamics and Convective Diffusion

Diffusive mass transport in an electrolyte solution without superimposed convection is relatively ineffective because of the low diffusion coefficients experienced in solvents of viscosities comparable to that of water. In usual dielectric

solvents the diffusion coefficient of a low molecular weight species is similar to that in aqueous solution, which is of the order of approx. $10^{-5} \text{ cm}^2 \text{ s}^{-1}$.

Moreover, diffusion alone is typically a non-steady process that means on extension of time it proceeds with a steadily decreasing velocity because concentration gradients tend to level off. Figure 5.1 a demonstrates this, depicting schematically the temporal development of concentration profiles of metal ions in front of a cathode on which the metal ions are deposited with time-independent current density, i , in presence of supporting electrolyte of high concentration, which allows for metal ion diffusion alone, excluding mass transport by migration.

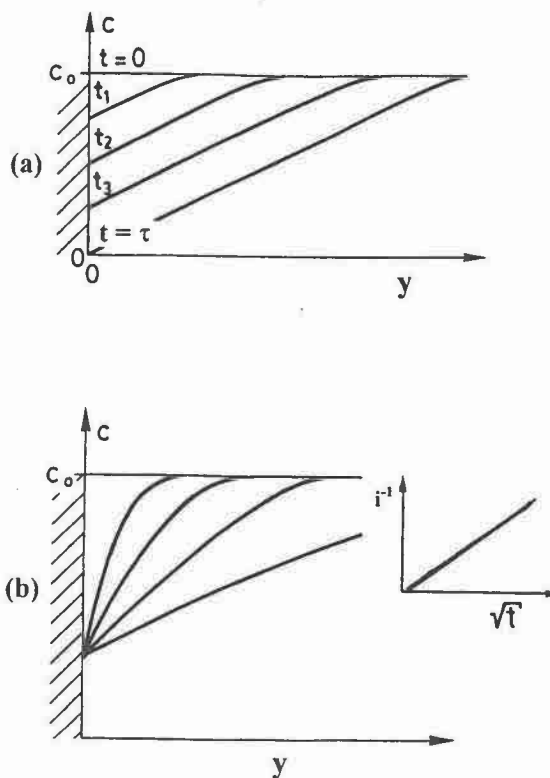


Fig. 5.1.a Schematic showing the development of concentration profiles of metal ions in a stagnant electrolyte upon galvanostatic cathodic metal deposition ($M^{z+} + ze^- \rightarrow M$). Note that $(dc/dx)_{x=0}$ remains unchanged because i is constant **b** Development of concentration profile of metal ions in stagnant electrolyte upon imposing a constant potential $\phi < \phi_{\text{equil}}$ on the electrode. Declining values $(dc/dy)_{x=0}$ reflect in steadily declining current densities according to $t^{-1/2}$ - law (see insert).

For a given current density i the gradient (dc/dy) is fixed at the electrode surface ($y=0$).

For metal ion reduction,



one obtains

$$D\left(\frac{dc}{dy}\right)_{y=0} = i/\nu_e F \quad (5.1)$$

and Fick's second law describes the change of the concentration profile in front of the electrode with time:

$$\partial c/\partial t = D\left(\partial^2 c/\partial y^2\right) \quad (5.2)$$

After the critical transition time τ the concentration of the metal at the electrode is depleted to zero and the mass flow $i/\nu_e F$ can no longer be maintained. Then the current will be consumed additionally by another electrode process, for instance by H_2 evolution with cathodic and O_2 evolution with anodic processes.

Therefore the electrode potential at $t = \tau$ will become so negative that hydrogen is evolved $H^+ + e^- \rightarrow 1/2 H_2$ parallel to metal deposition and hydrogen evolution would consume then larger and larger fractions of the applied current density with further extension of time.

Figure 5.2 b demonstrates, what occurs if a potential is applied to the cathode establishing according to Nernst's law a metal ion concentration c_0 being lower than c_∞ . Then a steadily decreasing current density for metal deposition will be observed. The developing concentration profile becomes flatter with time, $(dc/dy)_{y=0}$ and i is decreasing with time according to $t^{-0.5}$.

Imposed steady convection, and steady rates of electrochemical conversion expressed as time-independent current densities, generate steady concentration profiles and accordingly the one-dimensional Fick's second law, Eq. (5.2.), is substituted by the two dimensional steady state Eq. (5.3):

$$\partial c/\partial t = 0 = D\left(\partial^2 c/\partial y^2\right) - \partial(wc)/\partial x \quad (5.3)$$

y and x are coordinates perpendicular and parallel to the electrode and w is the flow velocity parallel to the electrode surface. Equation (5.3) is a simplified two-dimensional expression, which holds for one-dimensional flow parallel to the electrode (in x direction) and diffusive mass transfer due to metal deposition towards the electrode in y direction, i.e. perpendicular to the electrode surface (compare Fig. 5.2 a and b). Steady viscous flow along a planar surface generates a time independent velocity boundary layer and this, together with electrochemical conversion at the electrode, rules the spatial concentration distribution depicted in the

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