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The role of electrochemistry and electrochemical technology in environmental protection

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Abstract

For decades electrochemical technology has contributed successfully to environmental protection. In addition, environmental electrochemistry is capable of giving a huge contribution to further reach this goal by (1) application and improvement of existing technology, and (2) research, development and implementation of new technology. There is a tendency in the metal finishing and metal processing industries to redesign processes as closed loop systems. Therefore, we think especially the purification of dilute heavy metal ion-containing process liquids needs much of our attention. Electrochemical processes relevant to this purpose are considered and examples of (possible) industrial applications are discussed. Moreover, a critical evaluation of the usefulness of different types of electrodes is given. Generally, the two-dimensional electrode is the most favourable electrode configuration: the static flat electrode at high flow rates and in combination with mass transfer promoters, and the rotating disc electrode at high peripheral velocity. In both cases turbulent flow condition at the electrode are preferred to enhance the mass transfer. For redox systems where both the reactant and the product are soluble, the porous electrode is favourable due to its high specific surface area.

Keywords: Electrochemical processes; Regeneration of metal; Effluent treatment; Ion exchange assisted electrodialysis; Electroplating and surface finishing industry

1. Introduction

Electrochemical technology contributes in many ways to a cleaner environment and covers a very broad range of technology. Examples include generation of energy using (new) batteries [1] and fuel cells [2], selective synthesis of (organic) chemicals [3], removal of impurities from process liquids, air and soil, recycling of process streams [4] (e.g. from printed circuit industry) and sensors [5].

During the last two decades, a special research field, viz. environmental electrochemistry has been developed. Environmental electrochemistry [6–17] involves electrochemical techniques or methods to remove impurities from gases, liquids and soil to prevent or minimise environmental pollution.

In particular, emission to the atmosphere, discharges of pollutant into waters and disposal of solids to land sites have to be minimised. The best way to attack the problems is at their source, viz. mainly processes in the chemical and related industries. Environmental electrochemistry can contribute a great deal in reaching this goal. Especially, the purification of dilute heavy metal process liquids has been exhaustively investigated, since many heavy metals are very toxic and cause great environmental damage. Moreover, the reuse of metals needs more attention to prevent the disposal of heavy metal solid compounds in land sites.

The removal of heavy metals especially from dilute liquids is extensively discussed in this paper. Some attention is also paid to the purification of dilute gases and the removal of organics.

Dilute solutions to be purified are characterised by the:

- Nature of polluting inorganics (heavy metal ions) and organics.
- Concentration range of polluting species; mostly lower than 1000 ppm.
- Nature and the concentration of supporting electrolyte mostly lower than 1000 ppm and in some cases the concentration is some orders of magnitude higher.
- Specific conductivity of solution; mostly lower than $1\,\Omega^{-1}\,m^{-1}$.

Electrochemical removal of inorganics is obtained by direct electrolysis where only the reduction reaction is of interest, electrodialysis, and ion exchange assisted electrodialysis. To remove organics electrochemically from dilute solutions indirect electrochemical oxidation may be applied

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Nomenclature

a_e	specific electrode area (A/V) (m^{-1})
A	electrode area (m^2)
c_b	bulk concentration of selected species ($mol\,m^{-3}$)
c_i	inlet concentration of selected species ($mol\,m^{-3}$)
c_{min}	minimal concentration ($mol\,m^{-3}$)
c_o	outlet concentration of selected species ($mol\,m^{-3}$)
c_s	concentration of selected species at electrode surface ($mol\,m^{-3}$)
D	diffusion coefficient of selected species ($m^2\,s^{-1}$)
E	electrode potential (V)
f	rotation rate of the electrode (rps)
F	constant of Faraday ($96\,485\,C\,mol^{-1}$)
i	current density ($A\,m^{-2}$)
$i_{eff,\,min}$	typical minimum effective current density ($A\,m^{-2}$)
i_L	limiting current density ($A\,m^{-2}$)
k_m	mass transfer coefficient ($m\,s^{-1}$)
k_s	standard reaction rate constant ($m\,s^{-1}$)
k_{app}	apparent reaction rate constant (–)
K	constant ($1\,mol^{1-\alpha_{app}}\,m^{3\alpha_{app}-3}$)
L_c	depth of a 3D-electrode (m)
M	molecular mass ($kg\,mol^{-1}$)
n	number of electrons in electrode reaction (–)
s_n	normalised space velocity (s^{-1})
$u_s = U_s$	superficial liquid velocity ($m\,s^{-1}$)
V	cell volume (m^3)
z_A	charge of cation (–)
z_B	charge of anion (–)

Greek letters

α_{app}	apparent reaction order (–)
γ	enhancement factor of the mass transfer (–)
δ_N	thickness of Nernst diffusion layer (m)
μ	mobility of ion in the bulk solution ($m^2\,V^{-1}\,s^{-1}$)
ρ	spacetime yield ($kg\,m^{-3}\,s^{-1}$)
ϕ	current efficiency
ϕ_{an}	current efficiency for anion
ϕ_{cat}	current efficiency for cation

in some particular cases. Direct electrochemical oxidation methods are industrially of very little or no interest. The reasons for their uselessness can be:

- Oxidation of organics at an electrode to CO_2 and H_2O is mostly a very slow electrochemical process and practically impossible.
- No cheap and inert electrode material is available, e.g. Pb corrodes slowly, and then the water will be poisoned by Pb-ions. Recently, borium-doped diamond electrodes [18] have been used; it seems these are very inert, but expensive.
- Charge per molecule organic species is very high.
- Cheap alternatives are available, e.g. adsorption by active carbon and thereafter burning and oxidation by H_2O_2 or O_3 in or not in combination with UV.

Dilute gases contain small quantities of pollutants (500–5000 ppm). Moreover, many pollutants poisoning the air, for instance CO, NO_x, NH_3 and H_2S are very difficult to oxidise or reduce on an electrode.

The main purpose of this paper is a critical review of the real possibilities of electrochemistry and electrochemical technology to remove heavy metals from waste liquids, especially those from electroplating and surface finishing industry. First, direct electrolysis (Section 2) is extensively discussed with its relevant process parameters. In this section results from a theoretical one-dimensional reactor model are discussed (Section 2.3). In addition, a review is given of different three-dimensional and two-dimensional electrodes (Section 2.4). In the next sections the following interesting electrochemical processes are discussed: indirect electrolysis (Section 3), electrodialysis (Section 4), and ion exchange assisted electrodialysis: a hybrid process (Section 5).

2. Direct electrolysis

The key parameters for an electrolysis in the removal of impurities are the current density i, current efficiency ϕ, and spacetime yield (or normalised space velocity). The cell voltage is generally not a dominant parameter in environmental electrochemistry. To apply direct electrolysis in the industry, the effective current density i_{eff} must be higher than a fixed minimum, mainly determined by investment costs. A rough-and-ready i_{eff} will be larger than $10\,A\,m^{-2}$, where $i_{eff} = \phi i$ and i is based on the electrode surface area projected perpendicularly to the direction of the electrical current through the solution.

The effectiveness of electrolysis for dilute solutions is strongly determined by the mass transfer of the species to be removed, the effective electrode surface area and the occurrence of electrode side reactions.

2.1. Mass transfer

Liquid convection, diffusion and migration can determine mass transfer. The liquid convection directed parallel to the electrode surface determines the thickness of the Nernst diffusion layer δ_N; outside this layer the concentrations of species can be assumed to be constant. A schematic representation of a concentration profile of a species reacting on the electrode surface is given in Fig. 1.

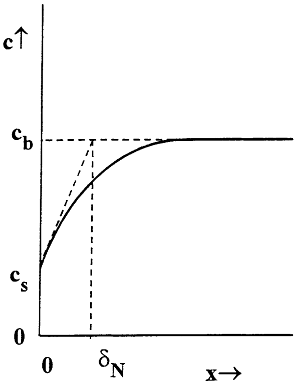

Fig. 1. A schematic representation of a concentration profile of a species reacting on the electrode surface.

If the concentration of the supporting electrolyte is a factor 10 higher than the concentration of the selected species to be oxidised or reduced, the migration of the selected species can be neglected. Its transport rate is then determined by diffusion and in stationary state given by Fick's first law:

$$i = nFD\left(\frac{\mathrm{d}c}{\mathrm{d}x}\right)_{x=0} \tag{1}$$

or

$$i = nFD\left(\frac{c_\mathrm{b} - c_\mathrm{s}}{\delta_\mathrm{N}}\right) \tag{2}$$

or

$$i = nFDk_\mathrm{m}(c_\mathrm{b} - c_\mathrm{s}) \tag{3}$$

where $k_\mathrm{m} = D/\delta_\mathrm{N}$.

The limiting diffusion current density is

$$i_\mathrm{L} = nFD\frac{c_\mathrm{b}}{\delta_\mathrm{N}} = nFk_\mathrm{m}c_\mathrm{b} \tag{4}$$

In the absence of supporting electrolyte migration as well as diffusion determine the transport of selected species. For solutions containing exclusively a 1:1 valency electrolyte the mass transfer coefficient of the cation is given by $k_\mathrm{m} = 2D/\delta_\mathrm{N}$. Generally, $k_\mathrm{m} = \gamma D/\delta_\mathrm{N}$, where $\gamma \geq 1$ and γ depends on the composition of solution. For a z_A:z_B electrolyte in the absence of supporting electrolyte for the migration of the cation the factor γ is given by [19]

$$\gamma = 1 + \left|\frac{z_\mathrm{A}}{z_\mathrm{B}}\right| \tag{5}$$

where z_A is the charge of the cation and z_B the charge of the anion as explained in Vetter [19]. For instance, assuming a dilute nickel sulphate solution contains $\mathrm{NiOH^+}$ and $\mathrm{HSO_4{}^-}$ species only, it follows that $\gamma = 2$.

Very different configurations of electrodes are applied in environmental electrochemistry. They can be divided into two groups, viz. the two-dimensional (2D-electrode) and the three-dimensional (3D-electrode) electrode. These electrodes can be used under static as well as moving conditions. In addition, turbulence promoters are used, in particular at the static 2D-electrodes. The mass transfer rate constant k_m is also determined by the solution convection caused by, e.g. forced solution flow through or along the electrode, rotation of electrode and gas bubble evolution on electrode.

Interesting electrode configurations in the environmental electrochemistry are given in Table 1. To norm the mass transfer rate constant k_m, its value is given for a $1 \times 1 \times 0.01\,\mathrm{m^3}$ cell with a projected electrode surface of $1 \times 1\,\mathrm{m^2}$. The flat-plate electrodes are placed in the 1×1 planes at a distance of 0.01 m and the 3D-electrode fills the whole cell. Estimated k_m values [8,10,13,20–24] are given for workable high mass transfer rate conditions. Moreover, for each electrode configuration a minimum concentration, c_min, where the electrolysis can be carried out on an industrial scale, is shown in Table 1. The minimum concentration c_min is based on k_m given in this table, $i_\mathrm{eff,\,min}$ is $10\,\mathrm{A\,m^{-2}}$ and $n = 2$. The current density $i_\mathrm{eff,\,min}$ is a typical minimum effective value proposed to use in industry.

Mass transfer to a membrane is similar to mass transfer to an electrode. This situation occurs in conventional electrodialysis cells. This type of electrochemical technology often applied in industry and is well described in [8,10]. An electrodialysis stack containing a great number of anion

Table 1
Interesting electrode configurations and corresponding transfer coefficients and minimum concentrations at industrially accepted conditions [8,10,13,20–24][a]

Electrode	High mass transfer conditions ($\mathrm{m\,s^{-1}}$)	k_m ($\mathrm{m\,s^{-1}}$)	c_min ($\mathrm{mol\,m^{-3}}$)
Flat-plate electrode	$u_\mathrm{s} = 1$	1×10^{-5}	5
RCE[b]	$U_\mathrm{e} = 10$	1×10^{-4}	5×10^{-1}
High-porosity 3D-electrode			
Porous electrode (RVC; 100 ppi)	$u_\mathrm{s} = 0.1$	1×10^{-2}	5×10^{-3}
Low-porosity 3D-electrode			
Packed bed electrode (2 mm particles)[c]	$u_\mathrm{s} = 0.1$	2×10^{-4}	5×10^{-4}
Fluidised bed electrode (0.5 mm beads)	$u_\mathrm{s} = 0.01$	6×10^{-3}	1×10^{-2}

[a] c_min is based on k_m given. $i_\mathrm{eff,min}$ is $10\,\mathrm{A\,m^{-2}}$ and $n = 2$.
[b] Diameter and height 0.5 m.
[c] Rods with 1 mm diameter and 1.8 mm length.

and cation membrane pairs is common. The concentration of supporting electrolyte must be low. This means that the solution practically contains only the cation to be removed and anions. The rate of mass transfer to a membrane is comparable to that of a flat-plate electrode.

2.2. Spacetime yield and normalised space velocity

An important process design parameter, correlated with the specific investment costs, is the spacetime yield ρ of an electrochemical cell [25]:

$$\rho = a_e \frac{i\phi M}{nF} \tag{6}$$

in which a_e is the specific electrode area (*A*/*V*), i the current density, ϕ the current efficiency, M the molecular mass, and n the number of electrons in electrode reaction. Combining Eq. (6) and the formula for the limiting current density, Eq. (4), yields an important formula for the design of an electrochemical reactor for the purification of wastewater:

$$\rho = a_e M \phi k_m c_b \tag{7}$$

This formula for electrochemical reactor design shows that for a certain metal concentration c_b the product of specific electrode area a_e and mass transfer coefficient k_m should be as high as possible. It should be noted, however, that the spacetime yield of a reactor is dependent of the wastewater properties. Therefore, Kreysa [26,27] introduced the normalised space velocity to characterise reactor performance:

$$s_n = \frac{I\phi}{(c_i - c_o)VnF} \log\left(\frac{c_i}{c_o}\right) \tag{8}$$

where c_i and c_o are the concentrations of the reactant at, respectively, the inlet and the outlet of the cell. This figure of merit means the volume of wastewater (m^3) for which the concentration of the key reactant can be reduced by a factor 10 ($c_o = 0.1c_i$) during 1 s in a reactor volume of 1 m^3.

2.3. Potential and current density distribution

In cells with two flat-plate electrodes the electrodes are normally placed parallel to each other, while in cells containing a rotating electrode a static counter cylinder electrode is concentrically placed around the working electrode. This means that under industrial conditions, where the bulk of solution has a practically uniform composition, the potential and current distributions over each electrode are uniform.

For a 3D-electrode, the potential E and the current density i change continuously with increasing depth of electrode L_c. The potential and the current density are strongly related to each other. The $E - L_c$ and $i - L_c$ curves depend on many parameters.

Portegies Zwart [20] has calculated the potential and dimensionless current density profiles in a packed bed electrode for the Fe^{3+} reduction, where its rate is determined by both mass transfer and kinetic parameters. He has used a theoretical one-dimensional reactor model. Moreover, he has calculated the total dimensionless cathodic current density as a function of a great number of parameters, viz. three-dimensional cathode thickness, standard electrochemical rate constant k_s, mass transfer coefficient, potential driving force, apparent exchange current density, and concentration levels of Fe^{2+} and Fe^{3+}. There are two extremes, viz. the one where potential and current density profiles are determined by the kinetic parameters as well as the specific resistance of solution, and the other by the local mass transfer as well as the specific resistance of solution. It has been found that the solution conductivity particularly plays a very important role and strongly determines the effective thickness of a three-dimensional roll if the electrochemical kinetic parameters are of interest.

Experiments were carried out to reduce ferric ions in a sulphuric acid solution using an undivided GBC-reactor (Gas diffusion electrode packed Bed electrode Cell) consisting of a gas diffusion anode fed by hydrogen and a packed bed cathode of small carbon rods [20,28] (see Fig. 2).

The reduction reaction of ferric at the packed bed electrode is

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \tag{9}$$

and the oxidation reaction of hydrogen at the hydrogen gas diffusion anode is

$$H_2 \rightarrow 2H^+ + 2e^- \tag{10}$$

The macroscopic reduction rate in the GBC-reactor can be described using an *empirical* reaction rate equation with apparent reaction parameters:

$$r = Kk_{app}c^{\alpha_{app}} \tag{11}$$

This equation combines the microscopic effects of mass transfer and electrochemical kinetics on the reduction

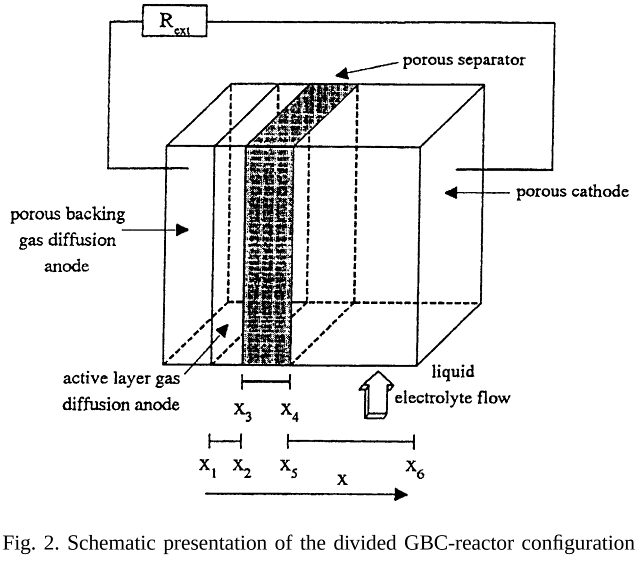

Fig. 2. Schematic presentation of the divided GBC-reactor configuration.

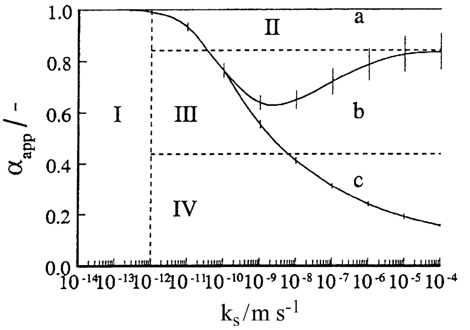

Fig. 3. Calculated apparent reaction order, α_{app}, as a function of the standard electrochemical reaction rate constant at different mass transfer rates. Roman numbers indicate different operating regimes (see text). k_m: 10^{-7} (a), 10^{-5} (b), 10^{0} (c) m s^{-1} ($k_m = k_{mO} = k_{mR}$).

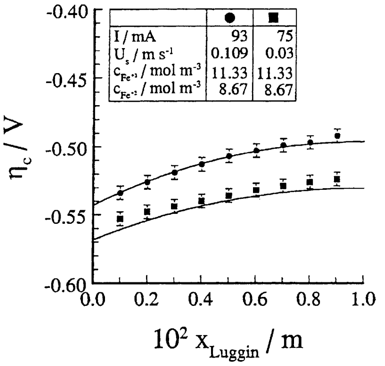

Fig. 4. Experimental cathode electrode potential profiles measured at different reactor current levels, superficial liquid velocities and concentrations of ferric and ferrous ions at $T = 313$ K. Drawn lines show results of numerical model simulations [20].

reaction into a macroscopic *apparent* reaction rate constant k_{app} and an *apparent* reaction order α_{app}. The parameter K is introduced as a constant, which has a value of 1 and a dimension of mol$^{1-\alpha_{app}}$ m$^{3\alpha_{app}-3}$, so that k_{app} has the standard dimension of m s^{-1}. Thus K only maintains the dimensional integrity of Eq. (11).

Portegies Zwart [20] has linked the results for the one-dimensional reactor model with experimentally obtained parameters using the aforementioned empirical reactor rate equation. He distinguished four zones in the $\alpha_{app} - k_s$ figure (see Fig. 3) for α_{app}, viz. $\alpha_{app} = 1$ at $k_s < 10^{-13}$ m s^{-1}, where the reduction process is kinetically controlled (zone I), $0.85 < \alpha_{app} < 1$ at $k_s > 10^{-13}$ m s^{-1}, where the reduction process is mainly determined by mass transfer (zone II), $0.45 < \alpha_{app} < 0.85$ at $k_s > 10^{-13}$ m s^{-1}, where the reduction process is determined by kinetics, mass transfer and ohmic effects (zone III), where α_{app} shows a very complex behaviour, and $\alpha_{app} < 0.45$ at $k_s > 10^{-13}$ m s^{-1} (zone IV), where very high mass transfer coefficient and standard electrochemical rate constant occur.

In zone IV, only the region of the 3D-electrode next to the gas diffusion anode is still active. It is very unlikely that this operating regime occurs in practice. For a kinetically limited process and a mass transfer limited process it is found that $\alpha_{app} = 1$, while k_{app} is, respectively, equal to the electrochemical rate constant for the reduction reaction or to the mass transfer coefficient. It has been concluded that the operating regime of the reactor can be identified using the values of α_{app} and k_{app} using the theoretical model. The model was used to optimise a GBC-reactor used for the regeneration of an electochemical machining electrolyte [20]. Apart from its apparent practical usefulness, this work serves as an illustration of how mathematical modelling can be used in electrochemical technology in general.

The potential profile over a RVC-cathode (reticulated vitreous carbon) in a GBC-reactor at the reduction of a 1 M H_2SO_4 solution containing small concentrations of ferric and ferrous was determined experimentally using a moving Luggin capillary. The potential profile was calculated using the one-dimensional reactor model. The results are given in Fig. 4. The agreement between the experimental and theoretical potential profiles is reasonable [20].

2.4. Different electrode configurations

The industrially interesting electrode configurations, given in Table 1, are discussed: first 3D-electrodes and then 2D-electrodes. Their advantages, disadvantages, and possible applications are presented and some experimental results are given. The authors are limited by the scope of the article and, also, their knowledge about not all electrodes discussed is enough to be able to produce an elegant little essay on each. However, a critical review is given. For more detailed information and also for application in commercial reactors see for instance [7,8,10,25].

2.4.1. Fluidised bed electrode

The fluidised bed electrode is a dynamic, 3D-electrode. A schematic representation of a fluidised bed electrode reactor used in practice is given in [10]. AKZO Zout Chemie originally developed it and it was further developed by Billiton Research for the extraction and reclamation of metals.

Advantages are a high mass transfer coefficient and the possibility of continuous removal of metal deposit from the cell. Disadvantages are a non-uniform potential distribution over the bed; dissolution of metal deposit in the unprotected zones of the bed (where the electrode potential of the particles rises to the corrosion potential); particle–particle and particle current feeder agglomeration and formation of inactive zones; and preferential growth near and on the separating membrane. Also, metal concentrations below 2 mol m^{-3} are not effectively treated because dissolved oxygen will sharply decrease the effectiveness of metal removal.

An industrial application is removal of Cu^{2+} ions from high conductive process liquids [29]. Only metal–metal ion couples with $E_r \gg E_{r,H_2}$ can produce a successful process.

2.4.2. Low-porosity 3D-electrodes

The low-porosity 3D-electrode can be divided into packed bed and moving bed electrodes; in both types of electrodes each particle is continuously in contact with other particles of the bed. This is the essential difference between a fluidised bed electrode and a low-porosity 3D-electrode. In most cases the latter has a voidage of about 0.4–0.5.

The electrically conductive particles of the low-porosity 3D-electrode can have a broad range of geometry, for instance granules, rods, spheroids, microspheres, and fibres.

Two different configurations of electrode reactors with 3D-electrodes are well known, viz. the flow-through reactor, where the direction of electric current is parallel to the direction of the solution flow, and the flow-by reactor, where the direction of electric current is perpendicular to the direction of solution flow [30]. The latter configuration is the most appropriate one in the environmental electrochemistry. Schematic diagrams for cells with packed and moving bed electrodes are shown in [8]. The advantages, disadvantages and relevant industrial applications are given next.

Advantages are a high mass transfer rate, a high degree of conversion, and the possibilities of simple and cheap electrode material. Moreover, the effective bed thickness will be high at high solution conductivity. For reduction reactions, the whole bed can be kept at a potential lower than the corrosion or equilibrium potential.

Disadvantages are that the effective bed thickness is limited by solution conductivity and the deposition of solid material especially on the bed particles, in particular those closest to the counter electrode. In addition, the effective bed thickness is limited by the concentrations of the reactants and the deposition of solid material causes a 3D-electrode to behave like a 2D-electrode. Other disadvantages are: electrode dendrite formation on the bed particles closest to the counter electrode results in damage to the membrane or separator; the range of useful electrode materials is low; and that a high volumetric flow rate results in a high pressure-drop over the reactor.

Relevant industrial applications are reduction reactions in which the reactant and product are soluble (Fe^{3+}, O_2, ${CrO_4}^{2-}$). Only in some specific cases metal ion removal and metal recovery may be carried out successfully and economically. Unfortunately, the packed bed is generally not applicable in small galvanic plants.

The reduction of ferric ions [31], nickel ions [32], and of chromate ions [33] in sulphuric acid solutions have been investigated for a GBC-reactor with a hydrogen gas diffusion anode and a packed bed of graphite particles. It was found that the deposition of nickel in the graphite particle bed causes many problems.

2.4.3. High-porosity 3D-electrodes

The high-porosity 3D-electrode has a very high voidage, larger than about 90%, and it can be composed of various materials, for instance, perforated plates, expanded metal meshes, felts and foams. Reticulated vitreous carbon (RVC) has been used very often because of its open structure; RVC grade 100 ppi has a voidage of about 97%. High voidage is important as the effect of the specific conductivity of solution is much smaller for a high-porosity electrode than for a low-porosity electrode. Advantages, disadvantages and possible applications of high-porosity electrodes are comparable to those for low-porosity electrodes.

Carbon felt is a porous electrode material used in a number of commercial cells [8]. This material has the advantage of a high mass transfer coefficient. However, it is sensitive to plugging. It is applied in reactors to remove metal and for the electrochemical oxidations of organic waste.

The reduction of ferricyanide ions has been carried out successfully at a RVC electrode in a 1 M KOH solution containing $2\,mol\,m^{-3}$ ferricyanide [20]. It was found that under these conditions mass transfer determines the reduction of ferricyanide.

The reduction of chromate in a 1 M H_2SO_4 solution containing $0.4\,mol\,m^{-3}$ chromate on a RVC electrode in a short-circuited GBC-reactor with a hydrogen gas diffusion anode is determined by kinetic parameters [32]. It was found that gold metal is a more attractive cathode material for chromate reduction [20]. A suggestion has been made to cover the surface of RVC electrode with a thin layer of gold metal (i.e. 1 μm) [20].

Continuous research has indicated, however, that a large gold electrode was clearly etched in a GBC-reactor fed by rinse water from a chrome plating bath (Cr-concentration was about $0.9\,mol\,dm^{-3}$). Due to the corrosion of gold under these conditions gold is not useful as cathode material. A comparative study on the reduction of chromate has shown that H_2O_2 can be used very effectively to reduce chromate in very dilute chromate solutions. In addition, it will be economically profitable.

Scale up and design optimisation of a GBC-reactor with a RVC cathode and a hydrogen gas diffusion anode were carried out by numerical calculations for electrochemical regeneration of an ECM electrolyte containing 3 M $NaNO_3 +$ small quantities of Cr(VI), Cr(III) and Fe(III). This solution is used in the processing of an iron–chromium alloy [20].

2.4.4. Two-dimensional rotating electrode

The removal of metal via cathodic deposition is carried out industrially with a reactor containing a rotating cylinder electrode (RCE). This is usually comprised of an inner rotating cathode in turbulent flow and a concentrically placed cylindrical counter electrode. Examples of cells are given in [8,10]. The advantages, disadvantages, and relevant industrial applications are as follows.

Advantages are a practically uniform potential and current density distribution and high mass transfer rates. These rates are enhanced by rough metal crystallites acting as micro-turbulence promoters. A typical enhancement factor for mass transfer is about 10 under industrial conditions (see

Walsh in [8]). The mass transfer coefficient can be controlled by rotation rate, independent of liquid flow. In addition, there is a small gap between anode and cathode, which also reduces the cell volume. The continuous removal of deposit is possible. Cascade reactors with cells containing only one RCE have been developed.

Disadvantages are that the fractional conversion per pass in a single reactor is normally much less than 0.6 and continuous removal of deposit (metal and/or metal hydroxide) from the cylinder leaves particles in the solution and results in the re-dissolution of metal. Besides, hydroxide formation can occur for some metal ions, e.g. Ni. The diameter of the cylinder is limited, particularly for a divided concentric reactor.

Relevant industrial applications are redox couples with soluble compounds, e.g. Fe^{3+}, ${CrO_4}^{2-}$, for which it is very useful, and noble metal deposition from dilute solutions: Cu from 0.5 M H_2SO_4 [10], Ag from photographic bath [10].

2.4.5. *Two-dimensional flat-plate electrode*

The flat-plate electrode is the simplest configuration and is used in the well-known and simple filterpress cells, mostly with forced convection flow. To enhance mass transfer plastic mesh and fluidised glass beads are used. The advantages, disadvantages and relevant possible applications are indicated.

Advantages are that it is easy to build in the well-known and simple filterpress reactor as a three-compartment reactor; a practically uniform distribution of potential and current density; easy periodic removal of cathodes covered with a metal deposit from an open cathodic cell compartment; and reuse of cathode after removal of metal deposit. In addition, simple turbulence promoters (plastic mesh, fluidised inert particles) can be used: an enhancement factor for mass transfer can be about a factor 10.

Disadvantages include a relatively low mass transfer coefficient, the minimum concentration to be achieved is relatively high, viz. about $5\,\mathrm{mol\,m^{-3}}$, and formation of hydroxides in solutions with typical metal ions, e.g. Ni. The conversion factor per pass for a single reactor is low and strongly related to the volumetric liquid flow rate though the reactor.

A possible industrial application is to keep process liquids on a low heavy metal ion concentration of about $2\text{–}10\,\mathrm{mol\,m^{-3}}$ by re-circulation of liquid through the reactor. In some cases a metal hydroxide deposit is formed, its adhesion to the electrode is weak.

The minimum attainable concentration strongly depends on the nature of the heavy metal cation to be removed, the composition of the supporting electrolyte and in particular on the pH and the presence of complexing ions.

The flat-plate reactor is not used on a large scale, also not in the traditional galvanic plating factories. This is probably due to the use of closed reactors, where the removal of the deposit is very time and labour intensive. To make this reactor more accessible an open cathode compartment in the filterpress cell will give new possibilities for applications.

2.4.6. *Gas diffusion electrode*

A gas diffusion electrode (GDE) has an electrically conductive high-porosity structure, where one side is in contact with the gas phase and the other with the liquid phase. To use the GDE in aqueous solutions it consists of two layers, viz. a thick hydrophobic layer, i.e. about 0.5–2 mm, and a thin hydrophilic layer, i.e. 0.1 mm, and containing an electrocatalyst to enhance the electrode reaction. This two-layer GDE is very useful to prevent leakage of water, so that the GDE is not flooded.

In principle, the GDE is a 3D-electrode, but under practical conditions it behaves like a 2D-electrode [20]. This means that the active electrode surface is located near the gas–liquid interface inside the GDE. Advantages, disadvantages and relevant industrial possibilities are as follows.

Advantages are a simple cell design, no aerosol formation, and a very high mass transfer coefficient. Attainable pollutant concentrations in air are very low, viz. 1 ppm (concentration of gaseous pollutants in waste gas streams is generally on the order of 500–5000 ppm).

Disadvantages are the activity of catalyst is very critical, a great sensibility to catalyst poisoning, and the relatively high costs of the GDE.

Possible industrial applications are the removal of electroactive gaseous compounds (Cl_2) [34], adsorption of inactive gaseous compounds (NH_3 in acidic solutions), and CO oxidation on a GDE loaded with platinum–rhutenium catalyst in phosphoric–tungstic acid mixture at high temperature (500 K). It has been found that nitric oxide oxidation with a GDE loaded with Pt-catalyst in 1 M H_2SO_4 is not possible in practice [35].

Long-term experiments have been carried out with the aim of removing NH_3 from air containing a large quantity of minute dust particles [35]. It has been found that the mass transfer coefficient decreases only slightly during a 90-day experiment. It may be possible that the application of GDE to remove gaseous components can be very successful.

3. Indirect electrolysis

Aqueous waste liquids from galvanic plants usually contain small concentrations of aromatic and aliphatic organic compounds, viz. less than $1\,\mathrm{mol\,m^{-3}}$. Generally, only a limited number of these compounds can be reasonably oxidised. Due to the very low concentration, electrochemical oxidation on an anode is not an economical option; in some cases only indirect oxidation using oxidators like ozone, Fe(III), hypochlorite, Ce(IV), Ag(II), bromine, and peroxides can be successfully applied. The use of metal oxidants is generally only acceptable for closed process liquid circuits to prevent metal losses. Other oxidants like ozone, hydrogen peroxide, hypochlorite and persulphate may be used in open-end circuits, since an excess of these compounds can be easily destroyed before the purified water is fed to open waters. The compounds can be produced either on-site in special electrochemical cells or in some cases directly in the process liquids. For instance, chloride can be effectively oxidised on noble metal–titanium electrodes and in alkaline solutions where hypochlorite is formed. Recently, it has been found that sulphate can be oxidised to persulphate with a high current efficiency on borium-doped diamond electrodes. This electrode material is promising because of its high chemical stability at extremely high electrode potentials, viz. higher than 2 V vs. normal hydrogen electrode.

4. Electrodialysis

Conventional electrodialysis is applied in industry and well described in [8,10]. An electrodialysis stack containing a great number of anion and cation membrane pairs is common. The concentration of supporting electrolyte must be low. This means that the solution practically contains only the cation to be removed and its anion. The rate of mass transfer to a membrane is comparable to that of a flat-plate electrode. If there is no or negligible concentration of supporting electrolyte, the mass transfer coefficient is $k_m = \gamma D/\delta_N$, with γ given by Eq. (5).

The mass transfer of the species becomes very complex at current densities higher than the limiting current. In this case, a simple electrodialysis cell is used, to describe the processes occurring at the membranes, viz. a cell divided into three compartments (cathodic, anodic and centre compartments) by a cation-selective membrane placed between the cathodic and the centre compartment and an anion-selective membrane placed between the anodic compartment and the centre compartment.

To maintain electroneutrality, water splitting occurs at the membranes where the central solution becomes alkaline in a layer adjacent to the cationic membrane and the central solution becomes acidic in a layer adjacent to the anionic membrane. The processes strongly affect the behaviour of electrodialysis when removing heavy metal ions from the solution in the central compartment. In the case of a nickel sulphate solution, a greenish $Ni(OH)_2$ deposit is formed on the cation-selective membrane, hindering the electric current flow through the cell at current densities higher than the limiting current density.

Electrodialysis can be successfully applied in the removal of heavy metal ions from dilute solution if current through the cell is clearly smaller than the limiting current. The minimum concentration given in Table 1 for a flat electrode is also useful for a flat membrane. In combination with convection promoters (mostly used in electrodialysis cells) a minimum concentration of $0.5\,\mathrm{mol\,m^{-3}}$ for two-valency ions can be reached.

The current efficiency for the mass transfer through the membrane is also very important. For non-selective membranes the current efficiency for an ion is equal to the transport number of that ion in the bulk solution. In the presence of a single compound, e.g. MA, the transport number for the M^+ ion is given by the $\mu_M/(\mu_M + \mu_A)$, where μ is the mobility of ion in the bulk solution.

For cation-selective membranes a current efficiency ϕ_{cat} higher than 0.95 can be attained and for anion-selective membranes a maximum current efficiency ϕ_{an} of about 0.90 can be obtained. Moreover, the selectivity of an anion-selective membrane strongly depends on the nature and concentration of the dissolved compound. For instance, $\phi_{SO_4} = 0.90$ for 0.1 M H_2SO_4, and 0.5 for 1 M H_2SO_4, and ϕ_{Cl} is about 0.90 for 1 M HCl. It has to be noticed that commercially available anion-selective membranes are destroyed in alkaline solution and its destruction rate increases strongly with increasing OH^- concentration. Outside the electrochemical field many investigators are using the so-called non-selective membranes. But most of these membranes, especially the inorganic membranes, have a charge depending on the pH of solution. However, its effect is practically neglected always, since mostly the average diameter of the pores inside the available membranes are too large, viz. >0.1 mm. Advantages, disadvantages and possible industrial applications to purify solutions containing heavy metal ions are mentioned.

Advantages are that a simple cell design is possible, electrode products can be controlled, and concentrated solutions can be obtained. In addition, cation-selective membranes have a high selectivity and easy removal of metal deposit from open cathode compartment is possible.

Disadvantages are a low mass transfer coefficient, high membrane and electrode surface area, danger for poisoning, fouling, and slogging of membranes, and that anion-selective membranes have a moderate selectivity.

Possible industrial applications are the removal of heavy metals, for instance Ni^{2+}, Sn^{2+}, $CrO_4{}^{2-}$, phosphite and hypophosphite, from dilute solutions and to concentrate these metal ions.

5. Ion exchange assisted electrodialysis

Ion exchange assisted electrodialysis is a combination of electrodialysis and ion exchange technique [36–39]. This process is similar to electrodialysis with the exception that a bed of ion-exchange particles is placed in the dilute (centre) compartment. The presence of the bed increases the conductivity of the centre compartment and allows for improved nickel separation. A schematic picture is given in Fig. 5 for the purification of a dilute $NiSO_4$ solution.

Transport of metal ions in the centre compartment occurs by two processes, viz. transport of adsorbed species over the surface of ion-exchanger via a hopping process and transport of 'free' species through the solution. Using a cation-exchanger that is very selective for $Ni^{2+}$and the transport of 'free' Ni^{2+} is negligible. On the contrary, sulphate ions are not adsorbed and only transport of 'free' sulphate ions to the anode compartment takes place. It has been found that a mixed bed consisting of anion-exchange particles is

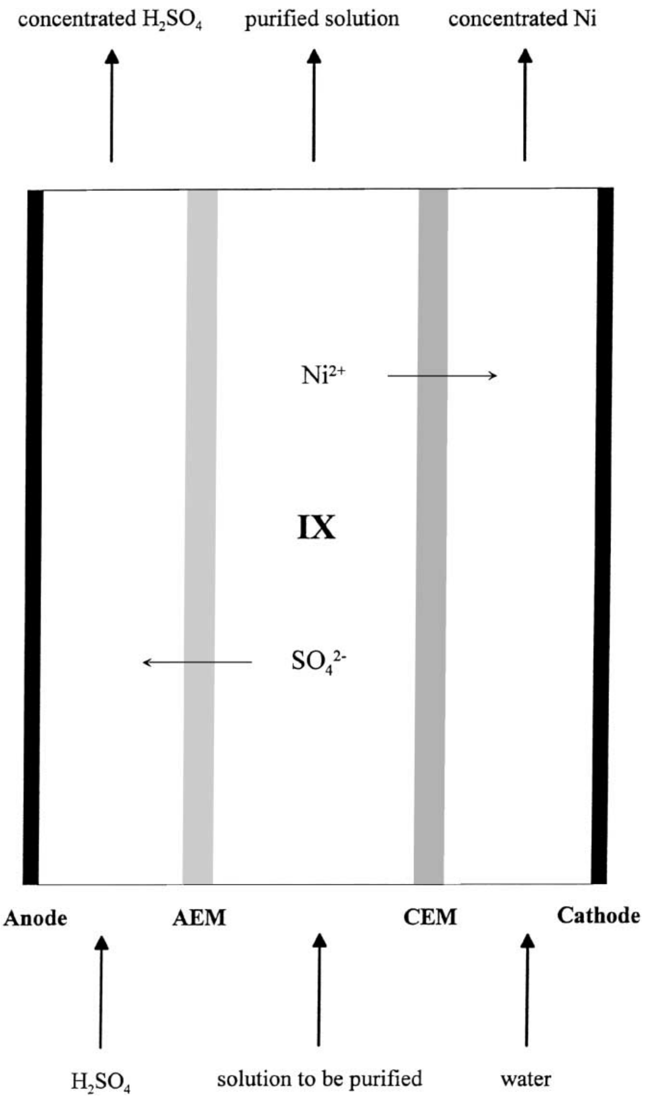

Fig. 5. Scheme of the ion exchange assisted electrodialysis set up.

not useful [8]. The possibilities of this new technique are now under investigation.

To remove heavy metal ions from a dilute solution, the electrodialysis cell is filled with a cation exchange absorber; organic resins are well known and inorganic adsorbers are also getting attention. It has been found that the use of two cation-exchange membranes instead of one cation-exchange and one anion-exchange membrane gives much better results using a resin bed already loaded with Ni^{2+} ions and H_2SO_4 solutions as anolyte and catholyte [40,41]. In this case H^+ ions are transported from the anodic to the central compartment to replace the Ni^{2+} ions transported to the cathode compartment. Moreover, the formation of $Ni(OH)_2$ precipitate and the destruction of the organic anion-exchange membrane can be prevented.

Recent studies show that a static bed of cation-exchange resin gives a strongly non-uniform current distribution in the cell when the centre compartment is continuously fed by a dilute $NiSO_4$ solution. Based on this result, a successful continuous process seems only possible using a moving bed of ion exchange resin, where a loaded resin is fed to the cell and partly unloaded resin leaves the cell. On the other hand, a successful discontinuous process for metal removal from a dilute solution can be set up.

For the removal of Cu^{2+} from a $CuSO_4$ solution the analogue process has been demonstrated [37]. The process used 6–10 kW of power per kg of recovered Cu with a current efficiency ϕ_{Cu} of about 30%. The dilute concentration was less than $1\,g\,Cu^{2+}\,m^{-3}$. A test of several months using industrial process liquid showed that the process could certainly be used in practice [37]. We expect we will also show this for nickel. Advantages, disadvantages, and possible industrial applications are given next.

Advantages are the continuous regeneration without extra chemicals and the relatively high current efficiency. The method is capable of cleaning dilute process liquids ($c_{min} \sim 10^{-2}\,mol\,m^{-3}$ or less). Disadvantages are the need of careful experimental/industrial design, selection of membranes and ion exchange resin, and choice of process parameters. In addition, the precipitation of solids lowers the efficiency of the process. However, there are no problems with more dilute process liquids. Possible applications in industries with processes involving heavy metal electrolyte solutions; even selective removal of metal ions will be possible.

6. Conclusions

Availability of new electrode and reactor materials (materials science), the invention and development of new and more effective cell designs (electrochemical engineering) will further develop the field of environmental electrochemistry. Moreover, processes have to be designed for more complex industrial liquids. In addition, mathematical modelling of electrochemical processes in combination with validation and critical evaluation of these models could aid the further development of the electrochemical technology.

To conclude we review some major points of this paper:

1. Heavy metals in dilute process liquids can be removed by direct electrolysis, normal electrodialysis, and ion exchange assisted electrodialysis. A minimum concentration of about $1\,mol\,m^{-3}$ is attainable for the first two methods and may be about $10^{-2}\,mol\,m^{-3}$ for the latter.
2. 2D-electrode configuration should be preferred.
3. The filterpress reactor with an open cathode compartment, from which the cathode with metal deposit can be removed easily, and the closed RCE reactor are the most useful for deposition of metal and/or metal compounds.
4. Much research has to be done to design optimum ion exchange assisted electrodialysis reactors.

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