1

Technical Scale of Electrochemistry

Klaus Jüttner
Karl-Winnacker Institute, Dechema e.v., Frankfurt an Main, Germany

1.1 Introduction ........................................ 3
1.2 Advantages and Disadvantages of Electrochemical Processes .... 4
1.3 Electrochemical Reaction Engineering .................... 5
1.4 Fundamentals ......................................... 6
1.4.1 Current Efficiency .................................. 7
1.4.2 Space-time Yield ................................... 8
1.5 Electrochemical Thermodynamics ......................... 8
1.5.1 Energy Yield ....................................... 11
1.5.2 Specific Electrical Energy Consumption .............. 12
1.6 Electrochemical Cell Design ............................ 12
References .............................................. 19

Encyclopedia of Electrochemistry. Edited by A.J. Bard and M. Stratmann
Vol. 5 Electrochemical Engineering. Edited by Digby D. Macdonald and Patrik Schmuki
Copyright © 2007 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. ISBN: 978-3-527-30397-7
1.1 Introduction

From an academic point of view, electrochemistry has become a written chapter in science history, manifested, for example, by the Nernst equation or the Butler–Volmer equation, to mention a few of the most common relations. The interest of the academic community in electrochemistry as a discipline of fundamental importance has gradually declined in recent years. Electrochemistry today presents itself as a strongly diversified field, which one would call “applied electrochemistry”, ranging from the study of electrode processes for synthesis of inorganic or organic compounds, energy conversion, sensor development, electroanalytic devices, electrolytic corrosion to solid-state ionics, and any kind of system where charge transfer is involved at an electrified interface between electronic and ionic conductors. Research is more and more specialized on very particular problems, often of a multidisciplinary character, being in touch with biology, medicine, microelectronics, structuring, and functionalizing of surfaces at the nanoscale as a part of materials and surface science.

Another view on “applied electrochemistry” is that of the electrochemical engineer. Electrochemical engineering has become an established discipline of its own, which deals with the description and optimization of electrochemical processes based on the fundamental laws of chemistry and electrochemistry. Essentially, it is an interdisciplinary field, which came up in the 1960s after the development of chemical engineering, providing the tools of unit operations for the systematic description and treatment of chemical processes in a way that linked the underlying physical and physicochemical principles to chemical technology. One of the pioneers was C. Wagner, who initiated this development by his article “The Scope of Electrochemical Engineering” in “Advances in Electrochemistry and Electrochemical Engineering” [1]. It soon became apparent that this kind of treatment can be adopted and transferred to the field of electrochemical reaction and process engineering [1–19]. Today, established technical processes include chloralkali electrolysis and related processes of hypochlorite and chlorate formation, electrowinning of metals like aluminum and magnesium from molten salt electrolytes, hydrometallurgy for electrowinning of metals like copper, nickel, zinc, and refining of cast metals, electro-organic synthesis of, for example, adipodinitrile as precursor for polyamide (nylon) production, electroplating in the...
galvanic industry, or electrophoretic coating in the automotive industry. The environmental aspect has become a major issue and a crucial factor in the development of industrial processes to meet the requirements of sustainable development. In this field, electrochemistry offers promising approaches due to its environmental compatibility and use of the electron as a “clean reagent” [20–28]. There is common agreement among scientists that electrochemically based processes will be of increasing importance in the future to meet the economic and social challenges resulting from urgent demands of low-grade raw materials’ utilization, energy savings, and protection of the environment.

1.2 Advantages and Disadvantages of Electrochemical Processes

Applied electrochemistry can provide valuable cost efficient and environmentally friendly contributions to industrial process development with a minimum of waste production and toxic material. Examples are the implementation of electrochemical effluent treatment, for example, the removal of heavy metal ions from solutions, destruction of organic pollutants, or abatement of gases. Further progress has been made in inorganic and organic electrosynthesis, fuel cell technology, primary and secondary batteries, for example, metal-hydride and lithium-ion batteries. Examples of innovative industrial processes are the membrane process in the chloralkali industry and the implementation of the gas-diffusion electrode (GDE) in hydrochloric acid electrolysis with oxygen reduction instead of hydrogen evolution at the cathode [28].

Figure 1 shows the cell room of the electrolyzer at Bayer Materials Science AG in Brunsbüttel, Germany.

The main advantages of electrochemical processes are as follows:

- **Versatility**: Direct or indirect oxidation and reduction, phase separation, concentration or dilution, biocide functionality, applicability to a variety of media and pollutants in gases, liquids, and solids, and treatment of small to large volumes from microliters up to millions of liters.
- **Energy efficiency**: Lower temperature requirements than their nonelectrochemical counterparts, for example, anodic destruction of organic pollutants instead of thermal incineration; power losses caused by inhomogeneous current distribution, voltage drop, and side reactions being minimized by optimization of electrode structure and cell design.
- **Amenability to automation**: The system inherent variables of electrochemical processes, for example, electrode potential and cell current, are particularly suitable for facilitating process automation and control.
- **Cost effectiveness**: Cell constructions and peripheral equipment are generally simple and, if properly designed, also inexpensive.

Since electrochemical reactions take place at the interface of an electronic conductor – the electrode – and an ion conductor – the electrolyte – electrochemical processes are of heterogeneous nature. This implies that, despite the advantages mentioned earlier, the performance of electrochemical processes suffers from mass-transport limitations and the size of the specific electrode area. A crucial point is also the stability of cell components in
1.3 Electrochemical Reaction Engineering

Electrochemical reaction engineering deals with modeling, computation, and prediction of production rates of electrochemical processes under real technical conditions in a way that technical processes can reach their optimum performance at the industrial scale. As in chemical engineering, it centers on the appropriate choice of the electrochemical reactor, its size and geometry, mode of operation, and the operation conditions. This includes calculation of performance parameters, such as space-time yield, selectivity, degree of conversion, and energy efficiency for a given reaction in a special reactor.

Electrochemical thermodynamics is the basis of electrochemical reaction engineering to estimate the driving forces and the energetics of the electrochemical reaction. Predictions of how fast the reactions may occur are answered by electrochemical kinetics. Such predictions need input from fundamental investigations of the reaction mechanism and the microkinetics at the molecular scale [29–50]. While microkinetics describes the charge transfer under idealized conditions at the laboratory scale, macrokinetics deals with the kinetics of the large-scale process for a certain cell design, taking into account the various transport phenomena. The microkinetics combined with calculations of the spatial distribution of the potential contact with aggressive media, in particular, the durability and long-term stability of the electrode material and the catalysts.

Fig. 1 Cell room of the hydrochloric acid electrolyzer with GDE in Brunsbüttel [28] (photo: Bayer Material Science AG).
and current density at the electrodes leads to the macrokinetic description of an electrochemical reactor [3–5, 7, 9, 10, 12–18]. The relation between micro- and macrokinetics is shown schematically in Fig. 2.

The phenomenon of charge transport, which is unique to all electrochemical processes, must be considered along with mass, heat, and momentum transport. The charge transport determines the current distribution in an electrochemical cell, and has far-reaching implications on the current efficiency, space-time yield, specific energy consumption, and the scale-up of electrochemical reactors.

1.4 Fundamentals

In the following, similarities and differences in the fundamental description of chemical and electrochemical reactions are considered with a definition of symbols and signs [51, 52].

In general, a chemical reaction is written as the sum of educts $A_i$ and products $B_j$

$$\sum_i v_{A_i} A_i = \sum_j v_{B_j} B_j$$  \hspace{1cm} (1)

with stoichiometric coefficients $v_i$. The rate of the reaction is defined by

$$r = \frac{1}{v_{A_i}} \frac{d n_{A_i}}{dt} = \frac{1}{v_{B_j}} \frac{d n_{B_j}}{dt} \quad \forall \ i, j. \hspace{1cm} (2)$$

where the stoichiometric coefficients are by definition negative for the educts, $v_{A_i} < 0$, and positive for the products, $v_{B_j} > 0$. Taking into account that the mole numbers of the educts are decreasing ($d n_{A_i} / dt < 0$) and those of the products are increasing ($d n_{B_j} / dt > 0$), the reaction rate $r$ (mol sec$^{-1}$) is always a positive number ($r > 0$).

Electrochemical reactions are characterized by at least one electron charge transfer step taking place at the electrode/electrolyte interface. Therefore, the electron $e^-$ appears as a reactant in the reaction equation with its stoichiometric coefficient $v_e$

$$\sum_i v_{A_i} A_i + v_e e^- = \sum_j v_{B_j} B_j.$$  \hspace{1cm} (3)

Typical electrode reactions are given in Table 1.

Applying Eq. (2) to the reactant $e^-$, the reaction rate normalized to the geometrical
The rate of an electrochemical reaction which results from (4) and (5) shows that within a certain time the electrical charge \( Q \) (Faraday constant \( F \)) the electrode surface area \( A_e \) can be written as

\[
r = \frac{1}{A_e v_e} \frac{d n_e}{d t}
\]  

(4)

The number of moles \( n_e \) transferred within a certain time \( t \) can be expressed by the electrical charge \( Q_t = I t = A_e i t \) and the Faraday constant \( F = 96485 \text{ As mol}^{-1} \)

\[
n_e = \frac{Q_t}{F}
\]

(5)

The linear relation

\[
r = \frac{i}{v_e F},
\]

(6)

which results from (4) and (5) shows that the rate of an electrochemical reaction \( r \) (mol cm\(^{-2}\) sec\(^{-1}\)) is proportional to the current density \( i \) (A cm\(^{-2}\)), the sign of which is determined by the sign of the stoichiometric coefficient \( \nu_e \). It follows that the current density is negative (cathodic), if the electrode reaction describes a reduction process (e.g., Eq. 3), and positive (anodic) for an oxidation process (opposite direction).

Equation (6) is the differential form of Faraday’s law. The common expression is obtained by integration of Eq. (2)

\[
\frac{1}{v_p} \frac{d n_P}{d t} = \frac{1}{v_e} \frac{d n_e}{d t}
\]

(7)

when applied to the simplified electrode reaction \( v_R R + v_e e^- = v_P P \) with a single reactant \( R \) and product \( P \)

\[
m_P = \frac{v_P M_P}{v_e F} Q_t
\]

(8)

Here \( m_P \) and \( m_R \) are the mass and \( M_P \) and \( M_R \) the molar mass of \( R \) and \( P \), respectively. Owing to the sign convention of \( v_i \), the mass \( m_R \) in Eq. (8) is negative, indicating that \( R \) is consumed during the reaction \( (Q_t < 0) \).

A prerequisite for the validity of these equations is that only the considered reaction takes place at the electrode. In reality, side reactions can occur in parallel, the individual contribution of which is given by their current efficiency \( \Phi^e \).

### 1.4.1 Current Efficiency

The classical definition of the current efficiency \( \Phi^e \) is based on Faraday’s law and relates the mole numbers \( n_P \) of the product to that of the electron \( n_e \) consumed in the
electrochemical reaction.

\[
\Phi^e_p = \frac{m_P v_P F}{v_P M_P Q_t} = \frac{n_P / v_P}{n_e / v_e}
\]  

(9)

In that sense, \(\Phi^e\) is the “yield of charge” \(Q_t\) consumed in the course of the reaction. The current efficiency defined by Eq. (9) represents an average value. The differential or point current efficiency is defined by [17]

\[
\Phi^e_p = \frac{1}{v_P} \frac{dn_P}{dt} / A_e F
\]  

(10)

which is consistent with the definition of the partial current density of the product \(P, i_P = i \Phi^e_p\).

1.4.2

Space-time Yield

Another performance criterion, which is of particular importance for the calculation of capital investment and running costs of an electrochemical reactor is the space-time \(\rho_{st}\) yield, which is the amount of product \(m_P\) produced per unit of time \(t\) and reactor volume \(V_r\)

\[
\rho_{st} = \frac{1}{V_r} \frac{dm_P}{dt}
\]  

(11)

Substitution of \(m_P\) from Eq. (8) leads to the point space-time yield

\[
\rho_{st} = \frac{v_P M_P}{v_e F} \Phi^e a e_{el(F)}
\]  

(12)

which contains a design factor (the specific electrode area \(a_e = A_e / V_r(\text{cm}^2/\text{cm}^3)\)) and a reaction factor (the product of current density and current efficiency). It is evident that optimization will be directed toward enlargement of \(a_e\) and increase in the reaction rate, that is, the current density \(i\). The latter can be achieved, for example, by shifting the reaction from charge transfer to a mass-transport-controlled regime, where the diffusion-limited current density, as the maximum of the reaction rate, can be reached

\[
i_{d,\text{lim}} = -\frac{v_e}{v_R} F k_m c_R
\]  

(13)

This leads to the following expression:

\[
\rho_{st} = -\frac{v_P}{v_R} M_P \Phi^e a e_{k_m c_R}
\]  

(14)

In this case, \(\rho_{st}\) is proportional to the mass-transport coefficient \(k_m\), which can be increased by forced convection, for example, through agitation of the solution, enhanced electrolyte flow, turbulence promoters, or setting the electrodes in motion. Equations (12) and (14) are the key formula for the optimization of electrochemical cell design. Equation (14) is of particular importance for reactions with low concentrations, for example, recycling of metals from spent solutions or wastewater.

1.5

Electrochemical Thermodynamics

The Galvani potential difference arising at the electrode/solution interface, \(\Delta \psi = \psi_s - \psi_e\), depends specifically on the energy and density of electronic states in the two phases in contact. In principle, it is impossible to measure \(\Delta \psi\) at a single electrode. By combining two electrodes 1 and 2 to an electrochemical cell, the difference between the two interface potentials can be measured as the cell voltage \(U_c = \Delta \psi_1 - \Delta \psi_2\). To normalize this potential measurement, the standard hydrogen electrode (SHE) is used as a reference and the cell voltage \(U_c\) is denoted as electrode potential \(E\) versus SHE. The
1.5 Electrochemical Thermodynamics

The electrode potential at equilibrium, $E_o$, depends on the concentrations $c_i$ or activities $a_i$ of the reactants according to the Nernst equation

$$E_o = E^0 + \frac{RT}{v_F} \sum v_i \ln a_i$$  \hspace{1cm} (15)$$

where $E^0$ is the standard potential at $a_i = 1$, $T = 298$ K, and pressure $p = 1.013 \times 10^5$ Pa = 1013 bar. Table 1 contains the standard potentials $E^0$ of the selected electrode reactions. The standard potentials $E^0$ versus SHE or cell voltages $U^0_c$ can be calculated from thermodynamic data.

The standard Gibbs free energy of the overall cell reaction $\Delta G^0_{298}$ is related to the electrical work $nF U^0_c$.

$$\Delta G^0_{298} = -nF U^0_c$$  \hspace{1cm} (16)$$

which can be gained under quasireversible operating conditions of the cell, that is, at an infinitely low reaction rate.

$\Delta G^0_{298}$ is the stoichiometric sum of the Gibbs free energies of formation, $\Delta G^0_{f,i}$, of the reactants involved in the reaction

$$\Delta G^0_{298} = \sum v_i \Delta G^0_{f,i}$$  \hspace{1cm} (17)$$

In (16), $n$ is the number of electrons transferred in the overall process to maintain electroneutrality. Thermodynamic data for many chemical reactants and compounds are available as standard enthalpies $\Delta H^0_{f,i}$ and entropies $S^0_{f,i}$ from thermodynamic tables in handbooks, for example, [53, 54]. For the elements and for the proton $H^+$ (aq) in aqueous solution ($H_3O^+$), the $\Delta H^0_{f,i}$ values are zero by definition. Thermodynamic data for some typical electrochemical reactants are given in Table 2.

These data are related to the Gibbs free energy of reaction $\Delta G^0_{298}$ by the Gibbs–Helmholtz equation

$$\Delta G^0_{298} = \Delta H^0_{298} - T \Delta S^0_{298}$$  \hspace{1cm} (18)$$

where $T \Delta S^0$ is the reversible heat exchanged with the environment. The entropy change $\Delta S^0$ can be either positive or negative and is directly related to the temperature coefficient of the cell

$$\left(\frac{\partial U^0}{\partial T}\right)_p = -\frac{1}{nF} \frac{\partial \Delta G^0_{298}}{\partial T} = \frac{1}{nF} \Delta S^0_{298}$$  \hspace{1cm} (19)$$

Tab. 2 Thermodynamic data of typical reactants [41]

<table>
<thead>
<tr>
<th>Reactant</th>
<th>State of aggregation</th>
<th>$\Delta H^0_{298}[kJmol^{-1}]$</th>
<th>$S^0_{298}[JK^{-1}mol^{-1}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>g</td>
<td>0</td>
<td>130.74</td>
</tr>
<tr>
<td>Cl$_2$</td>
<td>g</td>
<td>0</td>
<td>223.09</td>
</tr>
<tr>
<td>H$_3$O$^+$</td>
<td>aq</td>
<td>0</td>
<td>55.13</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>aq</td>
<td>-167.54</td>
<td>205.25</td>
</tr>
<tr>
<td>O$_2$</td>
<td>g</td>
<td>0</td>
<td>70.12</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>l</td>
<td>-285.25</td>
<td>41.65</td>
</tr>
<tr>
<td>Zn$^0$</td>
<td>s</td>
<td>0</td>
<td>-152.51</td>
</tr>
<tr>
<td>Zn$^{++}$</td>
<td>aq</td>
<td>-92.53</td>
<td>-106.54</td>
</tr>
<tr>
<td>HCl</td>
<td>g</td>
<td>0</td>
<td>5.69</td>
</tr>
<tr>
<td>C</td>
<td>s</td>
<td>0</td>
<td>186.79</td>
</tr>
<tr>
<td>CO</td>
<td>g</td>
<td>-110.5</td>
<td>198.0</td>
</tr>
</tbody>
</table>

(g: gas; l: liquid; s: solid; aq: aqueous solution of activity one)
The $\Delta G^o_{298}$ values are calculated from the stoichiometric sum of the enthalpies of formation $\Delta H^o_{f,i}$ and the entropies $S^o_{f,i}$ of the species involved

$$\Delta G^o_{298} = \sum_i v_i \Delta H^o_{f,i} - T \sum_i v_i S^o_{f,i}$$

(20)

If $\Delta G^o_{298}$ is negative, the reaction is exergonic and should occur spontaneously, otherwise it is endergonic and does not occur or occurs in the reverse direction only. The negative sign in Eq. (16) implies that the cell voltage or standard potential of an exergonic reaction must be positive. This calls for a definition of the cell voltage measurement. According to IUPAC [51], the cell voltage is the potential difference between the right half cell I and the left half cell II, as shown in Fig. 3. The direction of the electronic current in the outer electronic circuit is defined from left to right, which means that cathodic reduction must take place in half cell I and anodic oxidation in half cell II.

This is demonstrated by combining an oxygen electrode and a hydrogen electrode as the two half cells of an electrochemical cell. The half cell reactions are commonly formulated as reductions:

**Oxygen electrode:**

$$\frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2e^- = \text{H}_2\text{O} \quad \text{with} \quad E^o_{\text{O}_2/\text{H}_2\text{O}} = +1.229 \text{ V versus SHE}$$

(21)

**Hydrogen electrode:**

$$\text{H}^+ + e^- = \frac{1}{2} \text{H}_2 \quad \text{with} \quad E^o_{\text{H}^+/\text{H}_2} = 0.0 \text{ V versus SHE}$$

(22)

If the oxygen electrode is placed on the right and the hydrogen electrode on the left in Fig. 3, according to IUPAC convention, the electrode reactions must be written

$$\frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2e^- = \text{H}_2\text{O}$$

(23)

$$\text{H}_2 = 2\text{H}^+ + 2e^-$$

(24)

so that the sum yields the overall cell reaction and the electrons are cancelled.

$$\frac{1}{2} \text{O}_2 + \text{H}_2 = \text{H}_2\text{O}$$

(25)

For the example considered, the overall electron-transfer number in Eq. (16) is $n = 2$. 

**Fig. 3** Electrochemical cell for the definition of cell voltage measurement according to the IUPAC convention [51].
The cell voltage under standard conditions is the potential difference between the right and left half cell: 

\[ U^0_c = E^0_{O_2/H_2O} - E^0_{H^+//H_2} = 1.229 \text{ V}. \]

Since \( U^0_c \) is positive, the Gibbs free energy of the reaction is negative according to Eq. (16)

\[ \Delta G^o = -2.96485 \cdot (1.299 - 0) \text{ V} \cdot \text{A} \cdot \text{S} \cdot \text{mol}^{-1} \]

\[ = -237.160 \text{ kJ} \cdot \text{mol}^{-1}. \]

The cell reaction (25) occurs spontaneously and the cell delivers electrical work \( nFU^0_c \), which is utilized in \( \text{H}_2/\text{O}_2 \) fuel cells (see also Chapter 8). Calculation of \( \Delta G^o \) from thermodynamic data in Table 2 yields

\[ \Delta G^o = (\Delta H^o_{\text{H}_2\text{O}_2} - \Delta H^o_{\text{H}_2\text{g}} - \frac{1}{2} \Delta H^o_{\text{O}_2\text{g}})
- T(S^o_{\text{H}_2\text{O}_2} - S^o_{\text{H}_2\text{g}} - \frac{1}{2} S^o_{\text{O}_2\text{g}}) \]

\[ = (-285.25 - 0 - 0) - 298 \cdot (70.12 - 130.74 - \frac{1}{2} 205.25) \]

\[ = -236.603 \text{ kJ} \cdot \text{mol}^{-1}. \]

The reversible heat \( T \Delta S^o = -48.647 \text{ kJ} \cdot \text{mol}^{-1} \) is negative. It is released by the system and cannot be exploited as electrical work.

If the two half cells are arranged opposite with the hydrogen electrode on the right and the oxygen electrode on the left, the corresponding reactions are reversed and the overall process refers to the electrolysis of water with hydrogen and oxygen as the products. In this case, the cell voltage \( U^0_c \) is negative and \( \Delta G^o \) is positive. The reversible heat \( T \Delta S^o \) is positive and is taken up from the environment; the cell cools down in the course of the reaction. This effect can be compensated if the cell is operated at an increased cell voltage generating the corresponding amount of Joule’s heat in the system. The corresponding cell voltage is denoted as the thermoneutral voltage

\[ U_{\text{th}} = -\frac{1}{nF} \Delta H^o \text{ with } \]

\[ \Delta H^o_{298} = \Delta G^o_{298} + T \Delta S^o_{298}. \]

\[ (27) \]

It is interesting to note that, in contrast to chemical reactions, electrochemical cells can operate in principle against a positive \( \Delta G \) if an outer current source is applied, driving the electrons in the opposite direction. This is the principle of the secondary batteries and electrochemical power sources, which can be charged and discharged to accumulate and release electrical energy.

1.5.1 Energy Yield

The costs of electrochemical processes are closely connected to the energy efficiency or energy yield, which is either related to the change of the Gibbs free energy of the reaction \( \Delta G \)

\[ \gamma_G = \frac{\Delta G \Phi^e}{nF U_c} = \frac{U_{c,0} \Phi^e}{U_c}, \]

or to the thermal energy (enthalpy change \( \Delta H \))

\[ \gamma_H = \frac{\Delta H \Phi^e}{nF U_c} = \frac{U_{\text{th}} \Phi^e}{U_c}. \]

\[ (29) \]

Here \( U_{c,0} = -\Delta G/nF \) is the cell voltage at equilibrium, \( U_c \) is the actual cell voltage under current operation, and \( U_{\text{th}} \) is the thermoneutral voltage, Eq. (27), which permits isothermal operation.
1.5.2 Specific Electrical Energy Consumption

For solid or liquid products, the specific electrical energy consumed is usually mass related

\[ E_e = \frac{Uc}{\nu_p M_p \Delta \rho_e} (\text{J kg}^{-1}) \]  

(30)

1.6 Electrochemical Cell Design

Different electrochemical cells have been developed for various applications in the past. According to the criteria of high mass-transport coefficient \( k_m \) and/or large specific electrode area \( a_e \), as predicted by Eq. (14), these cells can be classified as [20]:

- Cells with relatively small electrode area but *improved mass transport* to increase \( k_m \) by setting the electrodes in motion or by applying turbulence promoters. Examples are the pump cell [55, 56], the Chemelec cell [57], the ECO cell [58–60], the beat-rod cell [61, 62], and cells with vibrating electrodes or electrolytes [63].
- Cells with *enlarged electrode area* in a small cell volume are found in the multiple-cathode cell [64], the Swiss-role cell [65], the extended surface electrolysis (ESE) cell [66], and the capillary gap cell [13, 67].
- Cells with *three-dimensional electrodes* providing *enlarged specific electrode area* and *improved mass transport* due to the specific fluid dynamics inside the three-dimensional structure are, for example, the porous flow-through cell [68], the RETEC (RETEC is a trademark of ELTECH Systems Inc., Cardon, Ohio) cell [15], the packed-bed cell [69–71], the fluidized-bed cell [72–76], and the rolling tube cell [77, 78].

Some of them are shown, for example, in Fig. 4(a–c).

The *pump cell* is the rotating analogue to the capillary gap cell [67]. Although this cell has not yet been employed on an industrial scale, it is interesting because of its operation principles. It consists of two static disc electrodes with current connections and a bipolar rotating disk in between. The electrolyte is pumped radially from the central tube to the outer circumference by the rotating disk. The advantage of this design is that the mass-transfer coefficient can be controlled independent of the flow rate and the residence time of the electrolyte.

The *Chemelec cell*, Fig. 4(b), uses a fluidized bed of glass spheres as turbulence promoters to improve the mass transport to the electrodes consisting of a series of closely spaced gauze or expanded metal sheet. The residence time and the degree of conversion per pass are relatively low because the flow rate has to exceed the fluidization velocity of the bed. This cell is therefore suitable for pretreatment or recycling operations and is commonly used in the electroplating industry for maintaining a moderate metal ion concentration in a recirculated wash-water tank.

High mass-transport coefficients are obtained in cells with a *rotating cylinder electrode* (RCE) and a small gap between the anode and the cathode, Fig. 4(a). High rates of mass transport are experienced in the turbulent flow regime, so that RCE reactors allow metal deposition at high speed, even from dilute solutions. RCE reactors have been operated at a scale involving diameters from 5 to 100 cm, with rotation speeds from 100 to 1500 rpm and currents from 1 A to 10 kA [79]. It
1.6 Electrochemical Cell Design

Fig. 4 (a–c) Electrochemical cell design [13].
Fig. 4 (Continued).
is possible to design RCE reactors with a scrapping device to remove deposited metal powder continuously from the cathode surface. The so-called ECO cell, Fig. 4(a), with a cascade of baffle plates around the rotating cylinder cathode, which prevent back mixing of the solution to a great extent, attains high degrees of conversion.

A cell with a special design is the beat-rod cell, Fig. 4(a), which was mainly used in small electroplating shops. Supported cathode rods slowly rotate within an annular type of chamber in the electrolysis tank. The rods strike one another so that the metal deposit is removed and settles as a powder at the bottom.

An efficient way of fitting large planar electrodes in a small volume is the design of the Swiss-role cell, Fig. 4(b). Thin metal foils are separated by a plastic mesh and wrapped around a central core. The ohmic drop within the thin metal foil is largely compensated by contacting the foils on the opposite side. The electrolyte flows axially through the electrode pack. Large space-time yields are realized and mass-transport conditions are favorable since the separator also functions as a turbulence promoter. Mesh electrodes wrapped around a perforated winding core lead to another version of the Swiss-role cell with radial flow. Cells with mesh electrodes instead of foils are known as extended surface electrode ESE cells. A commercial system of this type is the RETEC cell, which contains 6–50 three-dimensional cathodes as flow-through metal sponge electrodes [15]. The cell is used in closed water recycling systems in the electroplating industry with applications similar to those of the Chemlec cell, Fig. 4(b).

A simple three-dimensional electrode is obtained by using a packed bed of conductive particulate material through which the electrolyte is pumped. Numerous versions of packed-bed cells have been described in the literature [13, 68, 80–84]. The potential distribution and optimum bed depth for metal deposition, $Me^{2+} + 2e^- = Me$, was calculated as a function of the effective particle and solution conductivities $(\kappa_p, \kappa_s)$ [13, 20]. For rectangular cell geometry and fully developed diffusion limited current density within the particle bed, the following relation was found for the optimal bed depth:

$$h_{opt} = \sqrt{\frac{2\epsilon_{k_s}\Delta \eta}{a_{k_s}Fk_m\epsilon_{Me^{2+}}}}$$

(condition $\kappa_p \gg \kappa_s$) (31)

where $\epsilon$ is the voidage of the 3-D electrode structure and $\Delta \eta$ the overvoltage range of the prevailing limiting diffusion current density in the microkinetic polarization curve. According to Eq. (31), the optimal bed depth increases with decreasing metal ion concentration by an inverse square root dependence. This has led to the enviro-cell design depicted in Fig. 4(c), where the bed depth widens with decreasing concentration along the flow direction of the solution.

The principle of fluidized-bed electrolysis originates from Fleischmann and Goodridge [73]. It has been examined for different applications [72, 85, 86] and was applied on an industrial scale for metal recovery [75, 76]. The electrolyte flows from bottom to top through a bed of fluidized particles, which are charged via a feeder electrode. The advantage is that the particles are held in suspension, thus avoiding bed blockage by the deposited metal. Because the height of the cell is restricted to about 2 m for hydraulic reasons and the fluidization velocity has to be maintained at a relatively high level, short residence times and thus only a limited degree of
conversion per pass can be achieved. Continuous operation with recirculation of the solution and cascade arrangement of cells has therefore been used in practical applications.

Moving and circulating bed electrodes, also denoted as a spouted bed, are described in the literature [87]. As an example, the rolling tube cell is shown in Fig. 4(c) [77, 78]. In principle, this cell resembles the well-known plating process for piece goods, using slowly rotating barrels. The rotating drum is only partially filled with particles to achieve thorough agitation. This cell has proved to be especially useful for silver and gold recovery. Further developments of moving bed electrodes and their application can be found elsewhere [88].

In Fig. 5, the specific electrode area $a_e$ (cm$^{-1}$) of various electrochemical cells is shown as a function of a characteristic length (interelectrode distance or particle diameter). It can be seen that the electrochemical cells differ significantly in their specific area and characteristic length by orders of magnitude. At a current efficiency of $\Phi^e = 1$, the space-time yield is mainly determined by the product

$$a_e l = \frac{I}{V_t} = j^*.$$  \hspace{1cm} (32)

The quantity $j^*$ (A cm$^{-3}$) can be considered as a volumetric current density or a current concentration, also shown in Fig. 5 as a function of the characteristic length. Extremely high current densities, for example, 10 kA cm$^{-2}$ in the chloralkali electrolysis, can be applied only in a limited number of cases, the number of cells with high specific electrode area is restricted to cases of low current densities [13].

A special cell concept combining ease of construction and scale-up is the capillary gap cell, which is mainly applied in electro-organic synthesis, where low conductivities of the electrolytes are a major problem, Figs 6 and 7, [13, 28, 67, 89]. The cell consists of circular disk electrodes with a small interelectrode gap (1–2 mm) to minimize the ohmic voltage drop in the electrolyte. The electrolyte

Fig. 5 Specific electrode area $a_e$ and volumetric current concentration $j^*$ as a function of the characteristic length of different electrochemical cells [13].
enters via a central channel and is radially distributed between the circular disk electrodes. In the bipolar configuration, the disks are isolated from each other and connected at the end plates to the voltage supply. To avoid reconversion of the product at the counterelectrodes in the undivided cells, the disk geometry and flow velocity must be carefully tuned to ensure that the diffusion layer thickness, which increases along the radius, does not reach the counterelectrode. Although the scale-up of the stack height and number of disks is simple, the outer disk radius cannot be enlarged. A number of electroorganic processes with methoxylation reactions for production of, for example, anisaldehyde and tert-butylbenzaldehyde, were recently developed at BASF [90, 91] using a somewhat modified cell with
graphite felt electrodes. They were also successful in developing “paired electrolysis” with the simultaneous formation of valuable products at the anode and at the cathode. A methoxylation at the anode was combined, for example, with the reduction of phthalic acid dimethylester to phthalide, a valuable precursor in pest management chemistry [92].

$$\text{Anode : } R-C_6H_4-CH_3 - 4e^- + 2 \text{CH}_3\text{OH} \rightarrow R-C_6H_4-\text{CH(OCH}_3)\text{}_2 + 4 \text{H}^+$$

$$\text{Cathode : } C_6H_4(\text{COOCH}_3)\text{}_2 + 4e^- + 4 \text{H}^+ \rightarrow C_8\text{H}_8\text{O}_2 + 2 \text{MeOH}$$

Another cell design strictly directed toward minimization of the ohmic drop in the electrolyte, especially if gases are developed at the electrodes, is the zero-gap cell, shown in Fig. 8 [17, 93, 94]. The perforated electrodes are pressed directly onto the diaphragm by the current collectors providing optimum contact across the whole electrode area. However, uneven current distribution and voltage drop in the electrolyte as well as in the diaphragm cannot be avoided, as illustrated in Fig. 8. Zero-gap cells have been successfully used for alkaline water electrolysis [93, 94].

Another design that is used in chloralkali electrolysis, water electrolysis, and electro-organic synthesis [95–97] is the solid polymer electrolyte (SPE) cell, where an ion exchanger membrane, for example, Nafion®, serves as the electrolyte, Fig. 9. The microporous catalytic reaction layers are pressed directly onto the membrane with porous current collectors allowing transport of dissolved reactants and gaseous products into and out of the reaction layer.

The advantages of SPE technology are as follows: electro-organic synthesis without an additional supporting electrolyte, reduced energy demand for separation and recycling processes, and elimination of side reactions with the electrolyte at moderate reaction conditions with ease of process control.

The structure of the SPE electrolysis cell is similar to that of the membrane

![Fig. 8 Gas evolution and current distribution at perforated zero-gap electrodes [13.]](image_url)
1.6 Electrochemical Cell Design

**Fig. 9** Solid polymer electrolyte (SPE) cell with cation exchanger membrane Nafion® [13].

Anode with catalyst layer
Cathode with catalyst layer

Metal mesh
Bipolar plate

Anodic current collector
Cathodic current collector

Electrode assembly in polymer electrolyte membrane (PEM) fuel cell technology, which is described in detail in Chapter 8.

References

78. W. Götzellmann, *Galvanotechnik* 1979, 70, 596.