we are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists



122,000

135M



Our authors are among the

TOP 1%





WEB OF SCIENCE

Selection of our books indexed in the Book Citation Index in Web of Science™ Core Collection (BKCI)

Interested in publishing with us? Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected. For more information visit www.intechopen.com



Scale-Up of Electrochemical Reactors

A. H. Sulaymon and A. H. Abbar

Additional information is available at the end of the chapter

http://dx. doi. org/10. 5772/48728

1. Introduction

Electrochemical technology 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 electro synthesis, 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 [1]. The main advantages of electrochemical processes are:

- *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 micro liters up to millions of liters.
- *Energy efficiency*: Lower temperature requirements than their non electrochemical 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. The backbone of any electrochemical technology is the electrochemical reactor, therefore the perfect design and scale-up plays an important role in successful of this electrochemical technology [2].



2. The principal of similarity

Dimensional analysis as a basic concept underlying the theory of transport processes and chemical reactor is familiar to every chemical engineer in analyzing laboratory data for reacting systems, the various rate constants, transfer coefficients, transport properties and reactor dimension must be combined in such a way that dimensional consistency is maintained. Most engineers are familiar with the Buckingham theorem which may be considered a formal restatement of the requirement of dimensional consistency [3]

3. Scale-up philosophy

An electrochemical reaction can be conducted in batch or continuous (mixed/plug flow) mode. Further, the reactors can be operated with or without recycle. Further classifications are possible on the basis of flow arrangement (parallel/series flow) or electrical connections (monopolar/bipolar). The electrodes may be flat (2-dimensional solid electrode) or porous (3-dimensional) electrode. Three-dimensional electrodes are used when high surface area is desired to compensate for the inherent low current density of the process. The electrodes can be configured to be horizontally placed or vertically placed [4]. The philosophy of scaling-up chemical process units requires the values of corresponding dimensionless groups of the two units are similar [5]. Several similarity criteria have been defined to guide the engineer to scale-up a reactor [6]. The criteria normally employed in thermo chemical reactors are those of geometric, kinematic and thermal similarity between the reactors. In the case of electrochemical reactors an additional criterion necessary to define the scale-up is that of current/potential similarity. These four criteria are discussed below:

3.1. Geometric similarity

Geometric similarity is achieved by fixing the dimensional ratios of the corresponding reactors. However, for electrochemical reactors, this criterion cannot normally be met, as increasing the inter-electrode gap would give a high voltage drop and increased energy costs. Further, in 3D electrodes an increased electrode thickness may cause a decrease in the average electric potential and/or promote secondary electrode reactions [7]. Therefore, geometric similarity is usually sacrificed in favor of current/potential similarity in electrochemical reactors. Scale-up in electrochemical reactors is achieved by using multiple cells and reactor units [8].

3.2. Kinematic similarity

Kinematic similarity is concerned with the flow velocities within a system. In any continuous reactor, the gas and liquid flow loads, or more generally the Reynolds number govern the pressure drop, fluid hold-up and mass transfer capacity in the system [9]. Therefore it was desirable to maintain similar gas and liquid flow velocities through the corresponding reactors.

3.3. Thermal similarity

Thermal similarity implies matching the temperatures in corresponding portions of the reactors under comparison. This condition may be approached by temperature control through internal heat transfer surfaces and/or heat exchange with recycling reactants. Thermal similarity is difficult to maintain in the scale-up of electrochemical reactors due to the effect of Joule heating within inter-electrode dimensions of the order of millimeters. The method of providing cooling channels between cells (as in conventional fuel cell stacks) is not practical in other types of electrochemical reactor and in any case would defeat the purpose of the reactor design.

3.4. Current/potential similarity

Electrochemical reactors, unlike their thermo chemical or chemical counterparts, require electrical similarity and this is usually the most important criterion in the scale-up of such reactors. Electrical similarity exists between two units when corresponding electrode potential and current density differences bear a constant ratio [8]. This criterion necessitates a constant inter- electrode gap on scale-up. One factor normally employed to quantify the effect is the Wagner number (Wa), which may be defined as:

$$W_a = \left(\frac{k}{L}\right) \left(\frac{dV}{di}\right) \tag{1}$$

Where (k) is the electrolyte conductivity, V the electrodepotential, i the current density and L the characteristic length. For electrical similarity, the Wagner number in the two reactors should have the same value at all points being compared. In 3D electrodes, an inverse Wagner number qualitatively describes the current distribution in the system [10]. These sets are the rules to get uniform current distribution for scale-up. i. e. for reactors operating under kinetic control, better uniformity is obtained for a higher slope of polarization curve, larger conductivity of electrolyte (k in equation (1)), smaller characteristic length (L in the equation (1)) and lower average current density. The constraints of current/potential similarity require that the scale-up of electrochemical reactors to industrial capacity is usually achieved by:

- i. Fixing the inter electrode gap while increasing the superficial area of individual cells
- ii. Stacking individual cells in monopolar or bipolar multi-cell reactors (e. g. containing up to 200 cells)

4. Current and potential distribution in electrochemical reactor

4.1. Current and potential distribution in planar electrode

Many industrial electrochemical processes use channel flow between two plane, parallel electrode as shown in Fig. (1)

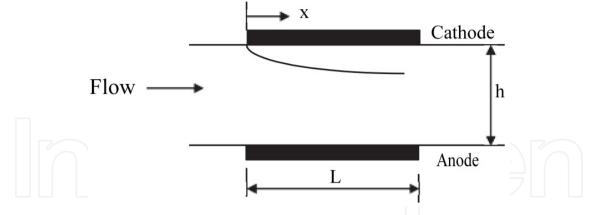


Figure 1. Parallel plate electrodes

The current distribution on such electrode is dependent on type of polarization occurring on the electrode surface; therefore current distribution can be classified as primary, secondary and limiting current distribution [11].

4.1.1. Primary current distribution

The primary current and potential distribution apply when the surface overpotentail can be neglected and the solution adjacent to an electrode can be taken equipotentail surface. Calculation of primary current distribution and resistance represents a first step toward analyzing and optimizing an electrochemical system. The cell resistance calculated can be coupled with calculation including mass-transfer and kinetic effects to optimize approximately a given cell configuration.

Calculation the primary current and potential distribution involves solution of Laplace's equation [$\nabla \phi = 0$]. Solution methods are analytically and numerically, the analytical methods involves the method of image [12],separation of variables [13], superposition [14,15], and Schwarz-Christoffel transformation [16]. The Schwarz-Christoffel transformation is a powerful tools for solution of Laplace's equation in systems with planar electrodes. This method was used by Moulten [17] which gave a classical solution for the primary current distribution for two electrode placed arbitrarily on the boundary of a rectangle, in their analysis they considered a special case of planer cells in which two plane electrodes placed opposite each other in walls of flow channel (Fig. (1)). The potential distribution is shown in Fig. (2) for L=2h. The current lines are represented by solid curves and equipotentail surface by dash curves. The two sets curves should be perpendicular to each other every where in the solution.

Moulten [17] represented the current distribution by the following equation:

$$\frac{i}{i_{av}} = \frac{v \cosh v / K (\tanh_2 v)}{\left|\sinh v - \sinh(2xv/L)\right|}$$
(2)

Where v = l/2h, x measured from the center of electrode ,(K)is the complete elliptic integral of the first kind tabulated in reference [18]. Primary current distribution is determined by

geometric factors alone, thus ,only the geometric ratios of cell are a parameter. Wagner number expresses the ratio of the polarization resistance at the interface over the ohmic resistance in the electrolyte approaches to zero in this case.

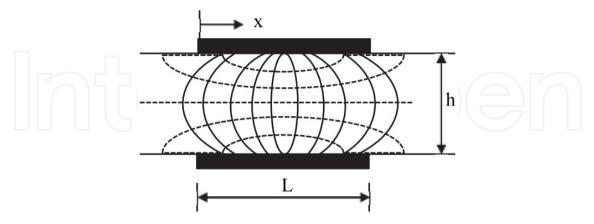


Figure 2. Current and potential lines in parallel plates electrode

4.1.2. Secondary current distribution

When slow electrode kinetics are taken into consideration, the electrolytic solution near the electrode is no longer an equipotentail surface, and the result of calculation is secondary current and potential distribution. Secondary current distribution predominates if the kinetic resistance is higher than the ohmic resistance. The general effect of electrode polarization is to make the secondary current potential nearly uniform than the primary current distribution and an infinite current density at the edge of electrode is eliminated. This can be regarded as the result of imposing an additional resistances at electrode interface [19]. Calculation of secondary current distribution was achieved analytically and numerically by several investigators [20]. The prediction of current distribution using numerical methods is an essential step in the rational design and scale-up of electrochemical reactors and in engineering analysis of electrochemical processes.

A numerical method for predicting current density distribution in multi- ion electrolytes was developed, assuming steady-state, 2D, dilute solution theory and constant properties. The parallel-plate electrochemical reactor (PPER) geometry was used. The calculation of current density for the PPER had been a frequent subject of study but reported mathematical models exist only for limited cases. For example, the models of Parrish and Newman [21] and Caban and Chapman [22] were based on the thin diffusion layer approach, while by Pickett [23] on the mass transfer control assumption, and those of White, Bain and Raible [24] and Nguyen, Walton and White [25] ignore axial diffusion and axial migration and do not account for high velocities

4.1.3. Tertiary current distribution

The combined effects of activation and concentration polarization give rise to changes in primary current distribution resulting in what is known as tertiary current distribution. In

such cases the potential of the solution does not obey the Laplace's equation due to concentration variation. When the concentration at surface of electrode approaches to zero, the limiting current condition occurs and distribution of current is limited by the mass transfer rate through the diffusion layer [26]:

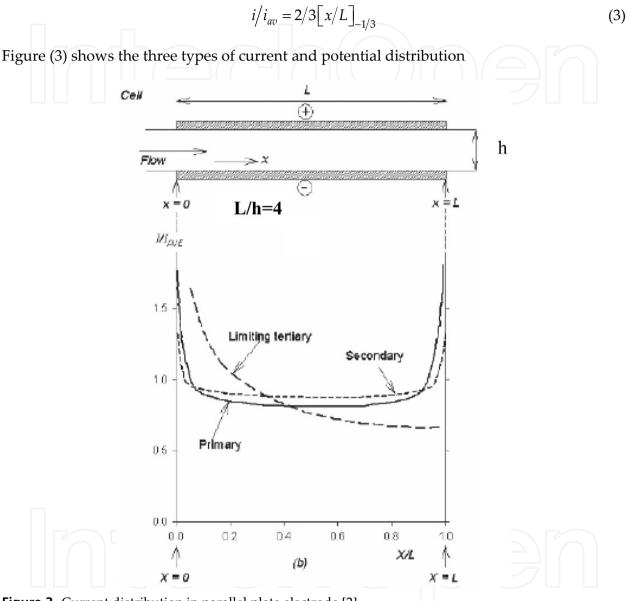


Figure 3. Current distribution in parallel plate electrode [2]

4.2. Current and potential distribution in cylindrical electrodes

Electrodes have been rotated at least since 1905 to provide some quantitative control of solution convection. Hydrodynamic theory for such electrode is generally considered to originate with Levich [27]. A number of rotating electrode geometries have been explored, namely the rotating cylinder electrode(RCE), rotating cone electrode, rotating hemispherical electrode, have been used, but only the RCE has grown to be generally accepted and increasingly widely used. Electrochemical reactors based on the RCE have particularly used

in metal ion removal from dilute aqueous solutions, where the metal can be deposited on the surface of an inner rotating cathode. The enhanced mass transport to such RCE cathodes has already been considered and a number of industrial devices have utilized this (and related) technology:

- i. The Eco-Cell [28, 29] and the Eco-Cascade cell [30]
- ii. The MVH cell [31]
- iii. The Turbocel [32]
- iv. A cell from Enthone±OMI [33]
- v. A rotating cathode band cell from Heraeus El-ektrochemie GmbH [34].

The design and application of RCE reactors in metal ion removal have been extensively reviewed [35, 36, 37]. The primary and secondary current distribution were studies by many investigators for example, the primary and secondary current distribution for deposition of copper–nickel alloys from a citrate electrolyte was studied by Madore and Landolt [38,39]where an empirical equation for the primary current distribution on rotating cylinder electrode has been reported as follows:

$$\frac{j_x}{j_{ave}} \frac{0.535 - 0.458 \times (x/h)}{\left[0.0233 + (x/h)^2\right]^{0.5}} + 8.52 \times 10^{-5} \times \exp\left[7.17 \times \left(\frac{x}{h}\right)\right]$$
(4)

Modeling of RCE cells has been focused on both the primary and secondary current distribution with very few studies of the tertiary current distribution.

4.3. Current and potential distribution in fixed bed electrodes

Packed bed electrodes can be used for electrochemical recovery of heavy metals from a variety of industrial and laboratory model solutions (Bennion and Newman [40]; Doherty et al. [41]; El-Deab et al. , [42]; Gaunand et al. , [43]; Lanza and Bertazzoli, [44]; Podlaha and Fenton, [45]; Ponce de León and Pletcher, [46]; Saleh, [47]; Soltan et al. , [48].

The study of the behavior of fixed bed electrode falls within the scope of electrochemical engineering considered to be the application of the principal of analysis and design of the chemical engineering discipline to electrochemical processes. Fixed bed electrode does not normally operate with a uniform reaction rate and potential, because of ohmic voltage losses within their structure and consequently the specific surface area is not used to full. From a practical point view, it is desirable to utilize most of the internal surface area of the electrode. The estimation of the utilized specific surface area is therefore of great importance in the design and scale-up of these electrodes and one approach is by analogy to the chemical engineering analysis of heterogeneous reactions such as gas–solid catalytic reaction and gas–liquid absorption with chemical reaction, extended to the electrochemical case. Therefore, an effectiveness or effectiveness factor is introduced into account for the fraction of bed thickness electrochemically reactive. This effectiveness (ε) is defined as follows:

$$\varepsilon = \frac{\text{observed electrolytic current for the desired reaction}}{\text{current obtained with an electrode whose over potential}}$$
(5)
is the same at every point for that reaction

As a rough guide to the operation of fixed bed electrodes, the effectiveness should have a minimum value of 0. 5 if they are to be considered worthwhile alternative to plate electrode cell [49].

Two principle configuration of fixed bed electrodes have been developed ,the flow through porous electrodes(FTPE) where fluid and current flow are parallel, and flow-by porous electrode (FBPE) where fluid flow perpendicularly to current [50]. The current and potential distribution in the first configuration is one-dimensional (the electrode potential varies in the direction of current flow) while the second type involving a two –dimensional problem(the electrode potential varies in the direction parallel to or perpendicular to current flow), which is inherently more complex than the first type.

In the first configuration, a dilemma can arise in choosing a sufficient electrode length to ensure a high conversion factor of the reacting species but avoiding at the same time, a too large potential distribution and consequently bad process selectivity. This is an obstacle for any tentative industrial application of the flow through porous electrode [51]. Alternatively in the second configuration the existence of two degree of freedom (thickness and length of electrode) make it possible to obtain simultaneously a uniform potential distribution and adequate residence time. Therefore this configuration is more adapted to an industrial use [52]. On the other hand, due to fact that first configuration obeys one-dimensional model ,it is very valuable in the theoretical formulations of current and potential distribution in porous electrode [53]. In addition Fedikiw [54] found that if the aspect ratio (length/thickness) of flow-by electrode is large, it is reasonable to assume that the potential field is governed by one dimensional Laplace's equation and consequently the flow through type can be considered to simulated the behavior of a horizontal slab of the flow-by electrode.

4.3.1. One-dimensional model

The complex structure of porous electrode is almost or always reduced for purpose of analysis to a one-dimensional representation. A one-dimensional model of porous electrode is most frequently used; this choice avoids considerable mathematical difficulty and at the same time provides solutions which are in reasonable agreement with experiment [55].

Coeuret et al. [56–58] were the first to study and analyse the current and potential distribution in flow through fixed bed by using a mathematical approach similar to that proposed by the chemical engineering discipline for heterogeneous reaction. They represented the current and potential distribution by the following dimensionless relationship:

$$\frac{\eta_{(X)} - \eta_{(o)}}{\eta_{(L)} - \eta_{(o)}} = \frac{\cosh\left[K_n(X/L)\right]}{\cosh(K_n) - 1} \tag{6}$$

Scale-Up of Electrochemical Reactors 197

$$K_{n} = \sqrt{\frac{n+1}{2} \frac{i_{o} zFSL^{2}}{RT\gamma} \left(\frac{\alpha}{\eta_{(L)}}\right)^{1-n}}$$
(7)

Where Kn is an effectiveness criterion for fixed bed electrode operating under Tafel polarization regime. Its value determines the effectiveness factor by the following relation:

$$\varepsilon_n = \frac{\tanh(K_n)}{K_n} \tag{8}$$

Where (εn) is the effectiveness factor for packed bed electrode under Tafel region.

It was found in scale-up of electrochemical reactor [59], the effectiveness factor (ϵn) for scaleup depends on bed thickness (L) and the potential at the back of electrode ($\eta(L)$). The conclusion was that effectiveness factor increases as bed thickness (L) decreasing and potential ($\eta(L)$) increasing.

Therefore a higher fraction of bed thickness reactive can be obtained either at lower thickness or higher value of potential. Practically, it is preferred to use higher thickness of bed to ensure a higher current supplied or production rate. On the other hand, it is necessary to utilize the maximum portion of surface area with maximum effective bed thickness. It is found that bed thickness not higher than 0. 6 cm must be taken as a maximum limit in the scale-up of the system under study and this system should not be operated beyond this value of bed thickness because it will be not utilized in the reaction zone and causing higher capital cost.

In recent years there are many researches have been done in scale –up of electrochemical reactor [60-62], the aim of these studies and the previous one are how to scaling up the electrochemical reactors to industrial case maintaining the same potential and current distribution. These factors have a vital role in developing the electrochemical system at different fields especially in waste water treatments.

4.3.2. Tow dimensional model

On the contrary to the one-dimensional model a few works have been concerned with the fundamental study of fixed bed electrode obeying two dimensional model. Alkire et al. [63] were the pioneers in the analysis of two dimensional model , where a finite difference method was adopted for Laplace differential equation solution. Their study was extended to the limiting current condition in subsequent work [64].

5. Mass transfer criteria for scale-up

5.1. Design equation for scale up of electrochemical reactor

The electrochemical cell can be controlled by mass transfer at the electrode surface. In the electrochemical cell, for example, a metal- ion concentration at the cathode surface

decreased by electrolysis. The mass flux of a metal-ion generated by a special concentration gradient can be described by Fick's law.

$$\dot{n} = -D \operatorname{grad} c \tag{9}$$

Equation (9) can be expressed in one-dimensional form which can be applied to diffusive mass transport for large flat electrodes:

$$\dot{n} = -D\left(\frac{\partial c}{\partial y}\right)_{y=0} \tag{10}$$

The current density of an electrochemical cell removing a metal-ion by electrochemical conversion couples the rate of electrochemical conversion with diffusive mass transport at and toward the electrode surface:

$$i = \dot{n}_0 v_e F = D \left(\frac{\partial c}{\partial y}\right)_{y=0} v_e F \tag{11}$$

The index 0 refers to y=0 which means at the electrode surface. The mass transfer rate and associated current densities are given by the product of the mass transfer coefficient km and the concentration difference:

$$i = n_0 v_e F = k_m (c_\infty - c_0) v_e F = k_m \Delta c v_e F$$
(12)

Setting C0=0 defines the mass transfer limited current density ilim:

$$i_{\rm lim} = k_m c_\infty v_e F \tag{13}$$

An explicit equation for the mass transfer coefficient, km, can be found for laminar flow. Under turbulent flow one can only measure the mass transfer coefficient by measuring the mass transport limited current densities. However, this is a tedious affair as mass transfer is often influenced by a great number of variables.

Dimensional analysis allows one to reduce the number of variables which have to be taken into account for mass transfer determination by introducing dimensionless groups. For mass transfer under forced convection, there are at least three dimensionless groups. Those are the Sherwood number, Sh, which contains the mass transfer coefficient, the Reynolds number, Re, which contains the flow velocity and defines the flow condition (laminar/turbulent) and the Schmidt number, Sc, which characterizes the diffusive and viscous properties of the respective fluid and describes the relative extension of the fluiddynamic and concentration boundary layer.

$$Re = \frac{wL}{v}$$
 $Sh = \frac{k_mL}{D}$ $Sc = \frac{v}{D}$

The experimental determination of Sh is quite easy in an electrochemical reactor. Measuring the limiting current and using equation (13), one obtains Sh from ilim.

Scale-Up of Electrochemical Reactors 199

$$Sh = \frac{i_{\lim} L}{c_{\infty} v_{\rho} FD}$$
(14)

In general, the dependence of Sh on Re and Sc can be presented in the form of a power series:

$$Sh = a R e^{b} S c^{1/3} \left(\frac{D_{C/A}}{L}\right)^{c} \left(\frac{D_{W/C}}{L}\right)^{d}$$
(15)

The design equation for the reactor scale-up is deduced by using dimensionless terms. Daewon et. al. [65] found that the dependence of Sh on Re, Sc, characteristic lengths, DC/A/L and DW/C/L could be described in the following form:

$$Sh = 1.24 Re^{0.12} Sc^{1/3} \left(\frac{D_{C/A}}{L}\right)^{-0.87} \left(\frac{D_{W/C}}{L}\right)^{-0.42}$$
(16)

Therefore the characteristic length plays an important role in scale-up of the electrochemical reactor in addition to Reynolds and Sherwood number.

Recently the performance of a novel pilot plant scale ,fixed bed flow through cell ,consisting of a cathode formed by a bundle of stainless steal tubes have been investigated [66]. Two mass transfer correlation which represented the flow in bandle of tubes have been obtained for two tube diameters(0. 6cm and 1. 0 cm):

$$Sh = 0.411 \text{ Re}_{0.871} \left[0.6 \text{ cm outer diameter tubs} \right]$$
(17)

$$Sh = 0.295 \operatorname{Re}_{0.84} \left[0.6 \operatorname{cm} \text{ outer diameter tubs} \right]$$
(18)

6. Conclusion

The design and scale-up of the electrochemical reactor play an important role in the development of industrial electrochemical processes. Therefore studying the controlling factors on scale-up make the operation of the system more efficient and economic on the commercialization stage. Current and potential distributions are the most significant parameters characterizing the operation of the electrochemical cell. The current density on the electrochemical process. In parallel plate and rotating cylinder electrodes, primary and secondary current and potential distribution are very important, the primary current distribution apply when the surface overpotentail can be neglected and the solution adjacent to an electrode can be taken to be equipotentail surface, while secondary current distribution predominates if the kinetic resistance is higher than the ohmic resistance. In porous electrodes, an effectiveness or effectiveness factor should be taken into account which refers to the fraction of bed thickness electrochemically reactive. The effectiveness should have a minimum value of 0. 5 if they are to be considered worthwhile alternative to plate electrode cell. Studding above factors in addition to the mass transfer correlation are

200 Electrolysis

an important parameter for scale-up the electrochemical reactor and should be considered in any future study in any electrochemical reactor before implant to industrial application.

Nomenclature

Ae	electrode area (cm2)	
С	metal concentration (mol cm-3)	
D	diffusion coefficient (cm2 s-1)	
Dc/A	gap between cathode and anode (cm)	
Dw/c	gap between reactor wall and cathode(cm)	
F	Faraday constant (96,487 C mol-1.)	
i	current density(A cm-2)	
<i>i</i> o	exchange current density (A cm-2)	
K_1	effectiveness criterion for linear polarization	
K_n	effectiveness criterion for Tafel polarization	
km	mass transfer coefficient(cms-1)	
L	thickness of screen or length of electrode (cm)	
M_{i}	molecular weight of chemical species i	
n	mass flux(gcm-2s-1)	
n ₀	mass flux at the electrode surface(gcm-2s-1)	
Re	Reynolds number	
S	scan rate	
Sh	Sherwood number	
Sc	Schmidt number	
Ve	stoichiometric coefficient of the electrons consumed in electrochemical reaction	
v	dynamic viscosity(g cm-1 s-1)	
W	linear velocity (cm s-1)	
W_i	deposited weight of chemical species i(g)	
Х	distance through the one-dimensional porous electrode(cm)	
Ζ	number of electrons	
Greek symbols		
	dimensional coefficient	

α	dimensional coefficient	

- ε effectiveness factor for linear polarization
- ε_n effectiveness factor for Tafel polarization
- η potential of cathode (V)

Author details

A. H. Sulaymon

Environmental Engineering Department, Baghdad University, Iraq

A. H. Abbar

Chemical Engineering Department, College of Engineering, Al Qadessyia University, Iraq

7. References

- [1] D. Hoormann, J. Jorissen, H. Putter, Chem. -Ing. -Tech. 77 (2005)1363–1376.
- [2] D. J. Pickett, Electrochemical Reactor Design, Elsevier, New York, (1977)12.
- [3] E. Buckingham, Physical rev. 4(2) (1914) 345.
- [4] C. L. Mantall, "Electrochemical Engineering"4th Mc-Graw Hill, New York, 1960.
- [5] R. H. Perry and C. H. Chilton, Chemical Engineers Handbook, 5thed. McGraw Hill, New York, (1973).
- [6] H. Rase, Chemical Reactor Design for Process Plants, Wiley-Interscience, New York, (1977).
- [7] D. Pletcher and F. Walsh, Industrial Electrochemistry, Chapman and Hall, (1990).
- [8] F. Goodridge and K. Scott, Electrochemical Process Engineering, Plenum Press, New York, (1994).
- [9] C. Oloman, J. Electrochem. Soc. 126(11) (1979) 1885.
- [10] G. Prentice, Electrochemical Engineering Principles, Prentice Hall, (1991)
- [11] C. Kadper, Trans. Electrochem. Soc. 78, (1940) 353, ibid, 82, (1942) 153.
- [12] J. Newmanm, J. Electrochem. Soc. 113, (1966) 501
- [13] J. J. Miksis, Jr. and J. Newman, ibid, 123, (1976) 1030.
- [14] P. Pierni and J. Newman, ibid, 126, (1979) 1348.
- [15] R. V. Churchill, "Complex variables and application", 2nd Mchrow hill, NewYork, (1960)
- [16] E. T. Copson"An introduction to theory of functions of complex variables" Oxford university press, London (1935)
- [17] H. Fletcher Moulton, Proceeding of London mathematical society, vol. (3)(1905), 104.
- [18] Milton A. Irene A., "Handbook of mathematical functions "Washington National Bearue of standard (1964) 608.
- [19] J. S. Newman, 'Electrochemical system''Prenti-hall, NewJersy(1973)
- [20] Prentice and Tobias, J. Electrochem. Soc. 129, (1982) 27
- [21] W. R. Parrish, J. S. Newman, J. Electrochem. Soc. 117 (1970) 43.
- [22] R. Caban, T. W. Chapman, J. Electrochem. Soc. 123 (1976) 1036.
- [23] D. J. Pickett, Electrochemical Reactor Design, Elsevier Science Publication Co, New York, 1979.
- [24] R. E. White, M. Bain, M. Raible, J. Electrochem. Soc. 130 (1983)1037.
- [25] T. V. Nguyen, C. W. Walton, R. E. White, J. Electrochem. Soc. 133(1986) 81.
- [26] J. S. Newman, I&EC, vol. 60, no. 4(1968), p. 12
- [27] V. G. Levich, 'Physiochemical Hydrodynamics', Prentice-Hall, New York (1962).
- [28] F. S. Holland, Chem. Ind. (London) (1978) 453.
- [29] Idem, UK patents 1 444 367 (1976) and 1 505 736 (1978);US patent 4 028 199 (1977).
- [30] F. C. Walsh, N. A. Gardner and D. R. Gabe, ibid. 12 (1982)299.
- [31] MVH Cell, van Aspert bv, Kastanjeweg 68, 5401 JP, Uden, The Netherlands.
- [32] J-Cl. Puippe, Oberfach. Surf. 32 (2) (1991) 17; EAST Re-port (1990), 38, E. G. Leuze Verlag. Saulgau, Germany;Galvano-Organo-Traitments de Surface 61 (1992) 259.
- [33] D. Hemsley, Prod. Fin. 46 (9) (1993) 5; idem, ibid. 47 (5), (1994), 6; idem, ibid. 47 (7), (1994), 9.

- [34] M. Mayr, W. Blatt, B. Busse and H. Heinke, Electrolytic Systems for Applications in Fluoride-Containing, Electrolytes, Fourth International Forum on Electrolysis in the Chemical Industry, (1990)..
- [35] N. A. Gardner and F. C. Walsh, in 'Electrochemical Cell Design', (edited by R. E. White) Plenum Press, NewYork (1984), 225.
- [36] F. C. Walsh and D. R. Gabe, I. Chem. E. Symp. Ser. 116(1990) 219.
- [37] C. T. J. LowmE. P. L. Roperts F. C. Walsh, Electrochim. Acta 52 (11), (2007) 3831-3840.
- [38] C. Madore, M. Matlosz, D. Landolt, J. Appl. Electrochem. 22 (12) (1992)1155.
- [39] C. Madore, A. C. West, M. Matlosz, D. Landolt, Electrochim. Acta 37 (1)(1992) 69.
- [40] D. N. Bennion, J. Newman, J. Appl. Electrochem. 2, (1972) 113–122.
- [41] T. Doherty, J. G. Sunderland, E. Roberts, ., D. J Pickett, Electrochim. Acta 41 (4), (1996) 519–526.
- [42] M. S., El-Deab, M. M., Saleh, B. E., El-Anoduli, B. G., Ateya, J. Electrochem. Soc. 146 (1), (1999) 208–213.
- [43] A. Gaunand, D. Hutin,, F. Coeuret, Electrochim. Acta 22 (1), (1977) 93-97.
- [44] M. R. V., Lanza, R., Bertazzoli, J. Appl. Electrochem. 30 (1), (2000) 61-70.
- [45] E. J Podlaha., J. M Fenton., J. Appl. Electrochem. 25, 299-306(1995).
- [46] C. Ponce de León, D. Pletcher, Electrochim. Acta 41 (4), (1996) 533-541.
- [47] M. M. Saleh, J. Phys. Chem., B 108, 13419-13426(2004).
- [48] E. A Soltan, S. A. Nosier, A. Y. Salem, I. A. S. Mansour, G. H Sedahmed, ., Chem. Eng. J. 91, (2003) 33–44.
- [49] J. S. Newman, W. Tiedemann, in: C. W. Tobias (Ed.), Advances in Electrochemistry and Electrochemical Engineering. Vol. 11: Electrochemical Engineering, John Wiley & Sons, New York, (1978) 353.
- [50] T. Risch, J. Newman, J. Electrochem. Soc. 131 (11), (1984) 208-213.
- [51] K. Scott, chemical engineering scence. vol. 37 (5), (1982)792.
- [52] M.. fleshmann, R. Jansson, Electrochemic. Acta, vol. 127(8), (1982)1029.
- [53] Kou-Chuan&J. Jore, J. Electrochem. Soc. 133 (7), (1986) 1394
- [54] P. Fedikow, J. Electrochem. Soc. 128 (4), (1981) 831.
- [55] F. A. Posey, J. Electrochem. Soc. 111 (10), (1964)1173.
- [56] F. Coeuret, D. Hutin, A. Gaunand, J. Appl. Electrochem. 6 (1976) 17.
- [57] M. Paulin, D. Hutin, F. Coeuret, J. Electrochem. Soc. 124 (2) (1977)180.
- [58] F. Coeuret, D. Hutin, A. Gavnand, Electrochem. Acta. 22 (1977) 93.
- [59] A. H. Abbar, A. H. Sulaymon, M. G. Jalhoom, Electrochimica Acta. 53, (2007) 1671–1679.
- [60] N. Gupta and C. W. Oloman, Journal of Applied Electrochemistry 36, (2006)1133–1141.
- [61] L. Szpyrkowicz and M. Radaell, Journal of Applied Electrochemistry 36, (2006) 1151–1156.
- [62] J. L. Nava, M. T. Oropeza, C. Ponce de León J. González-García, A. J. Frías-Ferre, Hydrometallurgy 91, (2008)98–103.
- [63] R. Alkire, N. Patrik, J. Electrochem. Soc. 121(1), (1974)95.
- [64] R. Alkire, N. Patrik, J. Electrochem. Soc. 124 (8), (1977)1220.
- [65] M. Daewon P., D. Chung and JU Jehbeck, Wat. Res. Vol. 35(1), (2001)57-68.
- [66] A. H. Sulaymon, A. O. Sharif, T. K. Al-Shalchi, J Chem Technol Biotechnol 86, (2011) 651-657.