



## Modeling in Electrochemical Engineering – A critical review

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### Abstract

In its 60 years life what has electrochemical engineering (ECE) contributed to society? Firstly, we have invented and developed processes to create new materials, more gently and more efficiently, so as to make life easier for all.

Secondly, ECE has changed our accepted concepts and our ways of thinking in science and technology. Here modeling stands out as the primary development. Let us consider this.

*Keywords:* Electrochemical modeling, electrochemical reactor, numerical analysis, simulation, optimization

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### Introduction

ECE is the branch of chemical engineering (ChE) concerned with the conception, design, and operation of electrochemical systems. Although the subject of electrochemistry has been known and studied for over 150 years, as a full-fledged wing of ChE, ECE came of age in the forties and fifties when the concept was realized that any electrode reaction, despite its characteristics, is amenable to the same kind of fundamental approach as is applied to heterogeneous catalysis. The second concept that delineated ECE as a branch of ChE is that the rate of electrode reactions is generally affected by the catalytic properties of the substrate of the electronic conductor as well as by the interplay of mass transport mechanisms that determine the diffusion rate of electroactive species. This review has been written predominantly to show chemical engineers that the design of electrochemical systems is an area entirely within their scope, and by no means as mysterious and difficult as is commonly supposed. It has also been written for electrochemists who are interested in finding out how the data can be used to design processes.

Today, electrochemical technologies are providing cleaner and more efficient energy for portable electronic applications,

vehicle propulsion and solutions to pollution problems. Batteries are an important part of our society today. Recent advances in portable electronics, laptop computers, and wireless communications have resulted in a significant growth in the need for small, high energy, reliable power sources. The research for new battery materials, exact simulation of existing electrochemical couples, or extending battery life are problems that could be solved by people trained in ECE fundamentals. Optimization of transport processes in porous electrode systems, advanced methods for the design and fabrication of electrodes, cells, and electrochemical systems, and the electrocatalysis of oxygen reduction and evolution are some of the current needs of ECE. In electrosynthesis, the generation of oxidizing chemicals for pollution control remains a viable field for exploitation. In addition, the removal of toxic impurities from lean waste streams by electrodeposition or oxidation of organic components remains attractive. The synthesis and characterization of new advanced materials for cathodes, anodes, and separators, and the mathematical modeling of the fundamental and diffusion processes occurring at the material-electrolyte interface are research topics of today in ECE.

ECE as an interdisciplinary subject may involve any of the following research areas: fundamental electrochemical studies at the electrode/electrolyte interface, mathematical modeling of the processes occurring at the electrode/electrolyte

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interface, methods of electrode preparation, corrosion behavior, and the life cycle of electrode materials and testing of materials. Other important areas of research include ionic mass transport by combined diffusion, migration, and convection, transport properties of concentrated, multi-component electrolytes, current distribution, and formation of new phases and modeling of composite processes in batch and flow systems. A careful review of these research areas in ECE with respect to ChE has been attempted.

The article is organized as follows. The electrochemical reaction modeling is presented first. Then models for electrochemical reactors (ECR) follow this, which can be done only if reaction model is available. Finally hybrid ECR models are discussed.

### Electrochemical Reaction Engineering

Electrochemical reaction engineering is an area which integrates the mechanistic, kinetic and transport behavior of electrode processes. In 1830's English scientist Michael Faraday studied the reactions which take place at the electrodes of electrolytic cells. He discovered the two laws which express the relationships between the amounts of products formed during electrolysis and the quantity of electricity passed. These can be conveniently combined in the following statement: The passage of 96487 coulombs through an electrochemical reactor produces in total one gram equivalent of products at an electrode. This quantity of electricity is called the Faraday and is designated by F. In the case of a number of reactions occurring at an electrode with  $n_j$  moles of  $j$  produced by a current  $I_j$  flowing for  $t$  seconds we can write,

$$\sum n_j = \frac{1}{F} \sum \frac{I_j t}{z_j}$$

where  $z_j$  is the number of electrons associated with the production of a molecule of  $j$ ,  $\sum n_j$  is the total number of moles produced.  $I_j$  refers to the partial current associated with the production of a given species. The total current  $I$  is evidently the sum of partial current.

Just as in chemical catalysis, electrocatalysis provides a reaction path which lowers the energy of activation and hence increases the rate of reaction, i.e., the current density for a given overvoltage. We can distinguish between the situation when a species in solution acts as a catalyst and a process where the reactive intermediate has to be adsorbed on the electrode. The epoxidation of propylene by means of bromide ions is a typical analysis. Pletcher [1], in his interesting book, Industrial Electrochemistry, demonstrates reasoning that can

sometimes lead to a decision on the most probable reaction path when an adsorption step is involved. Electrocatalysis is of major importance industrially. Use of dimensionally stable anodes in the chlorine industry is a good example [2].

### Electrode processes and reaction velocity

Based on the global concepts of heterogeneous chemical kinetics the difference between the rates of the forward (cathodic) and reverse (anodic) reactions of the general electrode reaction [3],  $A + ze^- \leftrightarrow B$  at equilibrium can be written as

$$i = zFk_{f_1} C_{A_s} - zFk_{b_1} C_{B_s}$$

By using an Arrhenius type of rate constant/activation energy relationship [4], the rate constants  $k_{f_1}$  and  $k_{b_1}$  can be expressed in term of the electrode potential, which is a measure of the free energy requirements.

$$k_{f_1} = k_{f_1}^0 \exp\left(\frac{-\alpha zF(-V_c^*)}{RT}\right) \text{ and } k_{b_1} = k_{b_1}^0 \exp\left(\frac{(1-\alpha)zF(-V_c^*)}{RT}\right)$$

The above equations imply that a fraction,  $\alpha(-V_c^*)$  of the cathode potential is effective in promoting the cathodic process, the remainder  $(1-\alpha)(-V_c^*)$  suppressing the reverse (anodic) process. At equilibrium,  $i = 0$  and the concentrations of A and B at the surface equals to bulk, thus we can easily manipulate the rate equation into the general form:

$$i = i_0 \left[ \frac{C_{A_s}}{C_{A_b}} \exp\left(\frac{-\alpha zF\eta}{RT}\right) - \frac{C_{B_s}}{C_{B_b}} \exp\left(\frac{(1-\alpha)zF\eta}{RT}\right) \right]$$

This is the Butler-Volmer equation [5]. It is a standard model that can be used to describe the current-overpotential relationship for an electrode at a specified temperature, pressure and concentration of reacting species. The overpotential  $\eta$  represents the departure from the equilibrium potential.  $i_0$  is the exchange current density represents the rates at equilibrium. An attempt to introduce some additional terms into B-V equation to allow elucidation of reaction mechanisms from current density/overpotential measurements is provided by the concept of an electrochemical reaction order due to Vetter [6]. A plot of the current-overpotential relation is commonly referred to as a polarization curve. For certain reactions B-V equation provides a reasonable description of current-overpotential behavior. Even when the reaction mechanism is known, it may not be possible to cast the overall current-overpotential relation in B-V form; in those cases an alternative simplified equation can often be developed. In the special case where the transfer coefficients are equal, the exponentials can be cast in the form of a hyperbolic sine function. When the magnitude of the overpotential is large,

another simplification is possible. If the overpotential is large and positive, then the first exponential term is much larger than the second term and the polarization expression becomes

$$\eta = \frac{RT}{\alpha zF} (\ln i_o - \ln i)$$

This expression is the Tafel equation. It is a good approximation to B-V equation for overpotential of more than 100 mV in absolute magnitude [7]. Polarization has three underlying causes: ohmic, activation, and concentration. Their effects are more or less addition and the potential shift is called an overpotential,  $\eta_{tot}$ .

$$E = E_{eq} + \eta_{tot}$$

$$\eta_{tot} = \eta_{ohmic} + \eta_{act} + \eta_{Conc}$$

The parameters that define the rate of a chemical reaction are determined generally by the broad area of the reaction, that is, chemical, photochemical, electrochemical, etc. In electrochemical reactions, the characteristic measurable parameter is the current density  $i$ , which is the current in A/m<sup>2</sup> of the electrode, and the parameter that converts it to molar rate is the Faraday. Thus the reaction rate (for the disappearance of A) if the case of cathodic reduction alone is considered can be expressed as [8]

$$-r_A = \frac{V_r}{A_c} \frac{dC_A}{dt} = \frac{i_A}{zF}$$

Alternatively the rate can be written as

$$\frac{i_A}{zF} = k_{f1} (C_{A_s})^m$$

where  $m$  is the order of reaction. The rate of reaction at an electrode surface is also governed by mass transport, defined through the use of a mass transfer coefficient  $k_{LA}$  for diffusing species A as

$$i_A = zFk_{LA} [C_A - C_{As}]$$

Eliminating surface concentration from the above equations the electrochemical reaction rate expression for a first order process becomes

$$\frac{i_A}{zF} = \frac{k_{f1} C_A}{1 + \frac{k_{f1}}{k_{LA}}}$$

Following the same procedure the reaction rate (assuming first order kinetics) for the general redox reaction after eliminating the surface concentrations of A and B can be expressed as

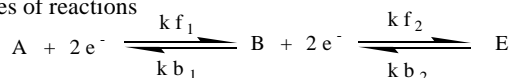
$$\text{Where } k_{f1} = k_{f1}^0 e^{-\alpha_1 fE}$$

$$k_{b1} = k_{b1}^0 e^{-\beta_1 fE}$$

This is a general and useful way of expressing electrochemical reaction rate of any redox reaction at an electrode [9].

### Complex electrochemical reaction schemes

Mathematical models of complex electrochemical reaction schemes are developed [10] in which mass transport of reactants and products at the electrode surface plays an important role in describing overall reaction rates. Cell operation is restricted to potentiostatic operation which allows the model solutions to be obtained in analytical form. The model can be used to simulate the behavior of a potentially useful organic synthesis like the electroreduction of oxalic acid to glyoxylic acid. Consider the reaction scheme for a series of reactions



The governing reaction rate equations in terms of kinetic and mass transfer parameters can be written in dimensionless form as

$$\dot{x}_A^b = -k_{mA}^* (x_A^b - x_A^s)$$

$$\dot{x}_A^s = \frac{zF}{k_{mA}} [k_{f1} C_A^b - k_{b1} C_B^s] + k_{b1} x_B^s$$

$$\dot{x}_B^b = k_{f1} \frac{k_{f1}}{k_{mA}} (x_A^b - x_A^s) - k_{b1} x_A^s$$

$$\dot{x}_B^s = -k_{mB}^* (x_B^s - x_B^b) + k_{f1} x_A^s - k_{b1} x_B^s - k_{f2} x_B^s + k_{b2} x_E^s$$

$$\dot{x}_E^b = k_{mE}^* (x_E^s - x_E^b)$$

$$\dot{x}_E^s = -k_{mE}^* (x_E^s - x_E^b) + k_{f2} x_B^s - k_{b2} x_E^s$$

Where  $x_i = C_i/C_{A0}^b$  is the dimensionless concentration of species  $i$ ,  $k_{fi}^* = ak_{fi} t^*$  and  $k_{bi}^* = ak_{bi} t^*$  for  $i = 1$  or  $2$ ,  $\dot{x}_i = dx_i/dt^*$  is the dimensionless reaction velocity, and  $t^* = t/t_f$  is the dimensionless time. The initial conditions become

$$x_A^b(0) = 1.0$$

$$x_i^b(0) = 0 \quad \text{where } i = B \text{ \& } E$$

$$x_i^s(0) = 0 \quad \text{where } i = A, B \text{ \& } E$$

By combining these equations to eliminate the surface concentrations, the reaction rates for both steps become

$$\frac{i_1}{n_1 F} = x_1 C_A^b + x_2 C_B^b + x_3 C_E^b$$

$$\frac{i_2}{n_2 F} = y_1 C_A^b + y_2 C_B^b + y_3 C_E^b \text{ and } i_T = C_{dl} \frac{dE}{dt} + i_1 + i_2$$

where  $x_i$  and  $y_i$  ( $i = 1, 2, 3$ ) are complex non-linear functions of the electrode potential, rate constants and liquid/solid mass

transfer coefficients [11]. Similarly by considering the reaction scheme for the parallel reactions, the reaction rates can be written.

One of the most striking questions of industrial importance is; what relationships exist between current efficiency and product yield? In view of the fact that any industrial process as a first step will correlate profit based on input and output. Thus the question may be answered in a further practical manner as follows

- No parallel reactions: current efficiency and product yield equal to 1.
- Electrochemical parallel reaction of reactant alone: current efficiency and product yield less than 1, but equal to each other.
- Chemical parallel reaction of reactant alone: current efficiency equals 1, product yield less than 1.
- Electrochemical and chemical parallel reactions of reactant: current efficiency and product yield less than 1, product yield is less than current efficiency.
- Electrochemical parallel reaction of another reactant alone: current efficiency less than 1, product yield equals 1.
- Electrochemical parallel reaction of the reactant and another reactant: current efficiency and product yield less than 1. Product yield is greater than current efficiency.
- Electrochemical and chemical parallel reaction of reactant, coupled with electrochemical parallel reaction of another reactant: current efficiency and product less than 1.

#### *Electrochemical reaction followed by series or complex chemical reactions*

The coupled chemical-electrochemical reaction sequence [12] is similar to that for the reduction of nitrobenzene (A) to the desired product p-aminophenol (D) and the undesired product aniline (U) through the intermediate phenylhydroxylamine (I). Here the reactant A is electrochemically reduced to a stable intermediate I which is itself a reactant for two competing parallel reactions: a homogeneous chemical decomposition to the desired product D, or a further electrochemical reduction to an undesired product U,  $A \xrightarrow{E} I \xrightarrow{C} D, I \xrightarrow{E} U$ . Taking into account the dynamic concentration changes at the electrode surface, the reaction rates are

$$\frac{dC_A^b}{dt} = -k_{mA} (C_A^b - C_A^s)$$

$$\frac{dC_A^s}{dt} = k_{mA} a (C_A^b - C_A^s) - k_{I_0} a e^{-\alpha_1 f E} C_A^s$$

$$\frac{dC_I^b}{dt} = k_{mI} a (C_I^s - C_I^b) - k_3 C_I^b$$

$$\frac{dC_I^s}{dt} = -k_{mI} a (C_I^s - C_I^b) + k_{I_0} a e^{-\alpha_1 f E} C_A^s - k_{2_0} a e^{-\alpha_2 f E} C_I^s$$

$$\frac{dC_U^b}{dt} = k_{mU} a (C_U^s - C_U^b)$$

$$\frac{dC_U^s}{dt} = -k_{mU} a (C_U^s - C_U^b) + k_{2_0} a e^{-\alpha_2 f E} C_I^s$$

$$\frac{dC_D^b}{dt} = k_3 C_I^b$$

Here  $C_i$  is the bulk concentration of the species  $i$ ,  $C_i^s$  is the concentration at the electrode surface, which differs from the bulk concentration  $C_i^b$  because of the presence of mass-transfer resistance,  $k_{mi}$  is the mass transfer coefficient of species  $i$ ,  $f = F/RT$ ,  $\alpha$  is the transfer coefficient and  $a$  is the specific electrode area. Only reactant A is present initially, which results in the initial conditions

$$C_A^b(0) = C_{A_0}^b$$

$$C_i^b(0) = 0 \quad \text{where } i = I, U \text{ \& } D$$

$$C_i^s(0) = 0 \quad \text{where } i = A, I \text{ \& } U$$

The analytical solutions of the above ODEs using the boundary conditions are given in [13] at steady state. The expressions obtained are suitable for use in reactor design, modeling and control. The other complex multiple reactions initiated by a charge transfer step at an electrode surface is anodic formation of chlorate and the epoxidation of propylene. For epoxidation of propylene, application of concentration profiling enables an accurate and straightforward analytical solution to be obtained.

A well-founded model of electrochemical engineering apparatus should be based on the equations of change for mass, energy and momentum. At present, the derivation of a model from the basic equation is an error prone and time consuming task normally requiring specific expertise. At the same time simulation techniques are gaining more importance in industry. This leads to an increasing gap between supply and demand of well-defined, consistent models. The expert system (ES) methodology commonly used in many engineering practice today give enough support for the modeler in the task of deriving a specific model. Extending the model library with electrochemical reaction models is also possible [14], but studies report only very few application specific ES.

We emphasize gain the need for reaction modeling. Because the plot of product formation as a function of mass transfer rate enables us to specify the required mass transfer characteristics of any cell intended to be used in a synthesis plant. A relatively simple model (if it is appropriate; some uncertainty in the numerical values of the model constants is not usually important) enables us to select the variables that govern performance. Experimentation, particularly at the expensive pilot plant stage, can be minimized and development costs significantly reduced. Development of a reaction model is an essential first step to obtaining a reactor model, which in turn is a must for process optimization [15].

### Electrochemical Reactor Engineering

In electrochemical terminology, the vessel in which electrochemical transformation occurs is called the cell. To bring the terminology in line with that of chemical reaction engineering, we refer to it as an ECR. An ECR is a device in which one or more chemical species are transformed to alternative states with an associated energy change. The electrochemical reactor unit can be made up of many cells which are suitably connected together both electrically and hydraulically. Factors that are important in the electrochemical reactor design are: productivity, energy requirement, cell voltage, temperature control, hydrodynamics, mass transport, reactor operation factors, electrode, membrane and other materials [16]. The form a reactor takes depends largely on the number of phases involved and the energy requirements. The size depends on the rate of reaction. It is the unique feature of ECR that the current and hence the reaction rate can readily be measured. The flux  $\mathbf{N}$  of any species  $j$  across a plane of cross-section area  $A$  is given by

$$\mathbf{N}_j = D_j \nabla C_j - \frac{z_j F}{RT} D_j C_j \nabla \phi + C_j \mathbf{u}$$

The bold-faced quantities in the above equation signify that they are vectorial; i.e., they have both magnitude and direction. The flux has the unit of  $\text{mol m}^{-2} \text{s}^{-1}$ .  $D$  is the diffusion coefficient  $\text{m}^2/\text{s}$ ,  $C_j$  is the species concentration  $\text{mol}/\text{m}^3$ .  $\nabla \phi$  is the potential gradient (i.e., the electric field  $\text{V}/\text{m}$ ),  $z_j$  is the ionic charge,  $\mathbf{u}$  is the solution velocity, and  $F$ ,  $R$  and  $T$  have their usual significance. We see that the overall flux and mass transport is driven by three terms: diffusion, migration and convection. The driving force for each of the three components is concentration, potential and density gradients respectively. Further, convection can be either natural or forced in an electrochemical system. Two other concepts related to the flow of charge and current flow are electrical conductance and

Table 1. Technical details for the selection of ECR

Factor	Choice A	Choice B
Mode of operation	Batch	Continuous
Number of anodes and cathodes	Single	Multiple
Electrode geometry	2-dimensional	3-dimensional
Electrode motion	Static	Moving
Electrode connections	Monopolar	Bipolar
Inter-electrode gap	Moderate	Capillary
Electrolyte manifolding	External	Internal
Cell division	Undivided	Divided
Sealing of cell	Open cell	Closed cell
Types of electrolyte	Liquid	Solid polymer

mobilities of both ionic and electronic species. For ECR, in general, the cell and electrode arrangements are so complex that specification of the velocity and concentration variations with time and location cannot be made. Thus, the requirement for the simultaneous solution of the convective mass transfer equation and the equation of motion (momentum transfer), even in the Navier-Stokes format (constant density and viscosity), cannot be met except in a few cases. Mass transfer analysis can be considered to proceed through one of three approaches. From theoretical or empirical analyses extensive complications of data on mass transfer have been correlated. These correlations usually employ dimensionless relationships from which mass transfer coefficients can be determined for the given geometric configurations and flow conditions. Some of the models for mass transfer coefficients are given in Table 1. Analogies between momentum and mass transfer have been developed through such approaches. The overall steps of the electrochemical process are shown in Fig 1. The technical information needed to choose an ECR are given in Table 2. It can be seen that decision 'B' will result in a greater effort in design, higher costs and also complex construction, however, provide operational flexibility. Although one tries to use undivided cells, diaphragms are sometimes essential. The voltage loss due to their presence can be greater than 10% of the total voltage loss in the cell. The effective conductivity  $\kappa_d$  of a diaphragm saturated with electrolyte can be predicted from knowledge of its hydraulic permeability  $p$  and its hydraulic radius  $r_H$ , for the relationship [17].

$$\frac{\kappa}{\kappa_d} = \frac{0.272 r_H^2}{p}$$

The foremost task of any engineering activity is the application of scientific knowledge to the obtention of

optimum results under the economic standpoint. Since the electricity required per unit of product greatly depends on plant size and design, optimization plays a vital role in electrochemical industries at large. Several optimization techniques have been reported in literature for the least-cost design of multi-product process. Optimization methods coupled with modern tools of computer-aided designs are also being used to enhance creative process of conceptual and detailed design of engineering systems. Genetic algorithms (GAs) are part of evolutionary computing, which is a rapidly growing area of artificial intelligence. Over last decade, GAs have enjoyed a large scale application for wide spectrum of engineering design problems [18]. But it has been seldom applied for optimizing electrochemical reactor. Vijayasekaran and Basha et al [19] are the first one to model ECR by GAs. The authors studied the effect of variables such as: current density, mass transport, reaction velocity, conversion, yield of the multiple reaction, and concluded that GAs found optimum results that satisfies both industrial practice and process economics. These results are encouraging and suggest the use of GAs in similar reactor design problems.

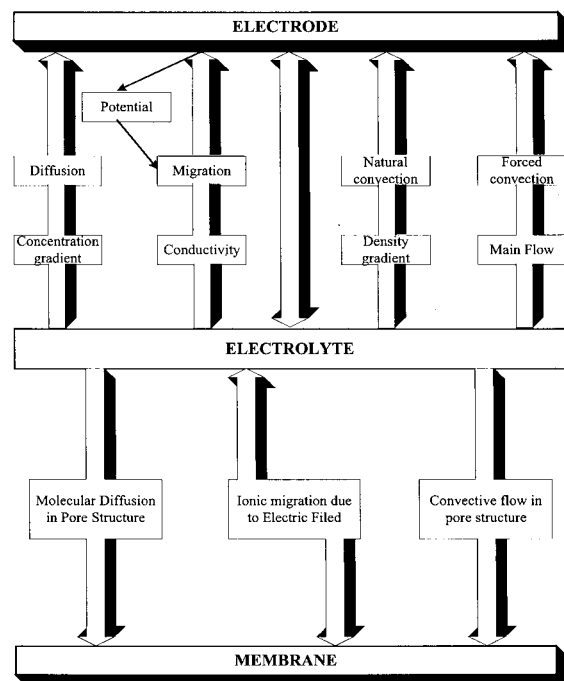


Fig.1. Schematic of ECR phenomenological sequences

Table 2. Models for Mass Transfer Coefficients

Model	Equation	Corresponding Exponents		Notes
		Re	Sc	
Film theory	$k = \frac{D}{t}$	-	1.0	Simple, Film thickness $t$ unknown
Penetration theory	$k = 2\sqrt{\frac{D}{\pi t_1}}$	0.5	0.5	Penetration time $t_1$ usually unknown
Surface renewal theory	$k = \sqrt{\frac{D}{\tau}}$	-	0.5	Renewal rate unknown
Eddy diffusivity	$k = \frac{D + E_D}{z}$	-	-	$E_D$ not calculable
Boundary layer theory	$k = 0.626 \frac{D}{L} \left( \frac{L \cdot v}{\gamma} \right)^{1/2} \left( \frac{\gamma}{D} \right)^{1/3}$	0.5	2/3	Derivable simple cases only (e.g. laminar flow past flat plate)

### Fundamental modeling concept

In ChE analysis of reactors, two particular models have great importance: the plug-flow model and the perfectly stirred flow tank model. The first model postulates that along the principal flow co-ordinate, the reactor axis, the concentration of reactants and products vary in a plug-wise manner: there is

no variation of concentration in any other spatial direction. The second model postulates that due to very efficient ("perfect") mixing, there is absolutely no spatial dependence of composition and the concentration of any species is uniformly the same everywhere in the reactor. The two models are very important; since they represent two extremes (no

mixing and perfect mixing), real reactors fall between the two limits defined by these two models. They can also describe real-life ECR with a reasonable accuracy. In a more realistic modeling, imperfect mixing in the flow tank and partial mixing in the plug-flow reactor will have to be considered, such an analysis of ECR requires rather sophisticated mathematical tools [20].

**Batch Reactor:** A batch reactor is charged with reactant, the required conversion takes place, and the reactor is emptied. One consequence is that the concentration of the reactant and products in the reactor are a function of time. There are two types of electrochemical batch reactors: those without electrolyte recirculation and those with recirculation. The former are suitable as laboratory devices for obtaining performance data as a function of electrode potential, reactant concentration, and hence conversion. The reactor is often run in a potentiostatic mode. The circulation is often used in industry because the recycle via a reservoir had the advantage of providing a flexible batch volume while the electrolyte flow through the reactor result in good mass transfer characteristic. Reactors are designed to have as uniform a current distribution as possible this condition is assumed in deriving reactor models. In case of a plug-flow batch reactor with recirculation using pseudo-steady state approximation, the expression for exit concentration of the reactant can be written as

$$C_A^f = C_A^0 \exp\left\{-\frac{t}{\tau_r} [1 - \exp(-ak_L\tau)]\right\}$$

For the case of stirred-tank batch reactor with recirculation, it is expressed as

$$C_A^f = C_A^0 \exp\left[-\frac{t}{\tau_r} \left(1 - \frac{1}{1 + ak_L\tau}\right)\right]$$

$\tau$  and  $\tau_r$  are the residence time in the reactor and reservoir respectively.

**Continuous Reactor:** Continuous reactors are confined to processes with large throughput. In the electrochemical field this means a small number of organic syntheses, continuous operation being largely confined to the inorganic field and effluent treatment. The problem of low conversion per pass is as evident in the continuous reactor as it was in the batch one. To meet sensible design requirements, a number of reactors have to be connected in series. Another way to get sufficiently high residence time is to operate the reactor with a recycle of the product stream. Models for a continuous reactor without recycle will be identical with those developed for the batch reactor. The design details of continuous plug-flow reactor with electrolyte recycle are described [21].

There exist certain fundamental characteristics of electrochemical reactors regardless of their size, shape, flow regimes, magnitude of current flow, voltage drop across electrolyte and other specific features: they are the material and energy balances, and the efficiency of a reactor in producing a given substance. Without their knowledge a reactor cannot be designed rationally and a process cannot be evaluated quantitatively.

### *ECR design*

Batteries and fuel cells constitute a major class of ECRs, in which stored chemical energy is converted directly to electrical energy. The engineering design of a battery or fuel cell is the culmination of a number of interdependent R&D efforts, each of which addresses application-specific requirements [22]. A typical set of tasks (many of which are conducted in parallel and rely upon the results of each other) common to the research, development and design of many batteries and fuel cells are (1) Electrode design – including size, shape, porosity, composition, catalyst dispersion, current collector structure, composition and fabrication method (2) Electrolyte composition – quantity including that in any reservoir and flow distribution (3) Cell dimension – Temperature and pressure. The designs of these cell components are chosen so that the electrochemical power source can meet its energy, power, durability and cost requirements. The fundamental thermodynamic, kinetic, transport and conservation principles are applied through mathematical modeling and/or experiments to derive cell voltage, cell current, efficiencies, current density distribution, temperature distribution, magnetic field distribution, species concentration, to assess phase formation/disappearance and the extent of side reactions.

The discharge of battery follows a sequence of processes, i.e., the discharge process begins when the adsorbed hydrogen at the surface of the active material reacts electrochemically with hydroxide ions, this consumption promotes formation of the hydrogen-depleted phase. Next, the adsorbed hydrogen that is consumed at the surface of the particle is replenished by diffusion of hydrogen atoms from the hydrogen-rich inner core through the outer hydrogen-depleted core to the surface. This is a typical phenomenological sequence that can be modeled based on classical ChE principles involved in modeling heterogeneous reactions in which a gas or liquid contacts a solid. Thus a quantitative criterion can be drawn about the discharge behavior of battery using progressive-conversion model or unreacted-core model [23]. Disappointingly, none

of the studies on batteries of any type has followed this approach. Such a model would help us understand the battery system better and may provide insight into the many issues like prediction of thermal runaway in lithium battery. For doing this, the heterogeneous reaction kinetics involved in chemical reaction engineering need to be understood along with mass transport philosophy.

Another major class of ECRs include reactor in which electrical energy is applied to electrochemically reduce or oxidize a chemical reactant. The same fundamental principles and set of tasks similar to those describe above for electrochemical power sources are applied to the design of this important class of ECR. Many of the requirements are satisfied in two general designs, based on either a tank electrolyser concept or a flow electrolyser concept.

Tank electrolysers are conceptually the simpler of the two types. In most cases the electrodes, either in the form of sheet, mesh or gauze is immersed vertically in the tank, arranged as alternate anodes and cathodes. This design has the advantage of being robust and allowing inspection of the cell contents and the electrodes. Electrowinning and electrorefining cell are the classic examples of tank electrolysers where the increase in size of the cathodes and their eventual removal and replacement make operation in any other form difficult. The tank electrolyser concept is restricted to processes, where there is no penalty paid for the relatively poor mass transport characteristic. This latter factor, together with low space-time yield, has tended to favor the adoption of flow cells using parallel-plate, three-dimensional and rotating electrodes in a large number of applications.

Flow electrolysers adopted in industry are frequently based on the parallel plate arrangement. There are practical (and economic) factors that limit the size of individual electrodes to areas of a few square metres, or less and thus electrochemical reactors are modular in design. The common design uses vertically mounted electrodes in a plate and frame configuration mounted on a mechanical press. Provisions for the use of membranes or diaphragms is usually made. A variety of reactor designs based on the concept of the parallel plate flow unit have evolved, some of which are Monsanto EHD, Asahi EHD, DuPont ESE and Ionic Chemomat [24]. These units have been designed by leading companies in the area of electro synthesis, and often in order to meet the requirements of specific reactions. All adopt bipolar electrical connection and external hydraulic connection, except the DuPont unit which uses an internal hydraulic connection. The general-purpose flow electrolysers currently available are DEM

(dished electrode membrane cell), ICI FM21-SP (arose from ICIs design experience from chlor-alkali membrane) and Electrocell AB, electrocell unit is a multi-purpose unit available in a wide range of sizes for scale-up [25].

Optimal control has for decades been a subject of academic research and industrial application. Optimal control theory was introduced four decades ago to calculate dynamic temperature-control strategies for chemical reactors to enhance reaction selectivity, but it has not been extensively applied to electrochemical reactors although static optimization of electrochemical processes is a well-discussed topic. Recent studies based on dynamic optimization methods, have shown that the traditional operating modes of batch electrochemical reactors, i.e. constant voltage or constant current, are not always the best [26]. This has been proved by determining the best transient operating profiles of control variables which optimize a specified performance index (cost functional or optimization criterion) subject to specified constraints if any. Unfortunately, in all these work the concentration dynamics of the various reacting and product species are ignored. One of the adverse effects of not taking into account the concentration dynamics is that the control may direct less quantity of desired product formation. Jayaraman and Basha [27] originally proposed the theoretical basis for writing reaction rate expression by taking account of concentration dynamics. They have applied the method for electrochemical reaction modeling in batch electrochemical reactors with/without recirculation. Thus optimal control problem statement itself should take into account this time-dependent concentration variation while calculating optimal profiles for the control variables.

#### *Current and potential distributions*

The aspect of current distribution can have a major effect on the performance of electrochemical processes [28]. A detailed analysis is outside the scope of this review although it is important to give a qualitative view of the effect due to its significance in design of ECR for industrial processes. In the case of cells with flowing electrolytes the unit is, by necessity, in some way open to the flow of solution and this therefore provides an additional electrical flow path at some peripheral position(s) on the electrodes. Thus as the current will tend to flow along the path of least resistance at these peripheral positions, it will be higher there. As in the case of the bipolar-connected electrodes, good cell design can minimize this effect. Thus in cells where the electrodes are not flush with the walls



or do not fill the complete cross-section, there will be a non-uniform distribution of current density.

Early analysis of current distribution considered the so-called 'primary distribution' i.e., the current distribution as determined by the Laplace equation in the absence of polarization or electrode kinetics. But the secondary current distribution is always more uniform than the primary one, since at those parts of the electrode surface where the current density tends to increase, the local overvoltage acts so as to suppress it. Calculation of the secondary distribution of current density require the knowledge of the parameters of the polarization curve for the studied electrode and of the specific electrolyte resistance, beside the geometric parameters of the cell. The combined effects of activation and concentration polarization also give rise to changes in the primary current distribution resulting in what is known as a 'tertiary current distribution'. In such case the potential of the solution does not obey Laplace equation due to concentration variations. Mass transfer theory must be applied to the reactor and the principles embodied should be examined. When gas bubbles are generated in electrochemical reactors their removal from the electrolyte is essential if conductivities are not to fall dramatically due to bubble accumulation. One of the first mathematical models describing the effect of the growth of gas fraction on the current distribution in a parallel plate electrochemical reactor is that of De La Rue and Tobias [29], there are a number of correlations now available to enable the prediction of this effect.

Several numerical or semianalytical solution techniques [30] are presented for solving Laplace's equation to obtain primary and secondary potential and current density distributions in electrochemical cells. But industrial electrochemical reactors are often operated under conditions that do not conform to either of the two limiting situations. In order to design a reactor exactly and also to understand the performance in this more complicated process, it is essential to take into account simultaneously of the several phenomena that influence the current distribution. Thus, it is necessary to solve for the concentration fields and the potential field simultaneously to obtain tertiary current distribution. The work done on current distribution in electrochemical reactors is sparse and that too on tertiary current distribution is very meager due to the complexity even with the existing computational facilities. But the calculation is needed, as the current distribution in electrochemical reactors is equally important as rate distribution in chemical reactors. This way of chemical engineering approach towards electrochemical

process design and development is not attempted. A numerical technique addressing this coupled phenomenon for all ranges of parameters will open up the possibilities for value-added electrochemical processes and synthesizing new chemicals. Furthermore, a non-uniform current density distribution may decrease the current efficiency of electrolytic processes.

### *Computational techniques*

Classical analytical techniques are Laplace transformation, separation of variables, conformal mapping, method of images, Green's function, perturbation, etc. However, analytical techniques are specific to the system, geometry and boundary conditions. Often times, analytical solutions involve integrals, eigenvalues, etc, which must be evaluated or obtained numerically. Even analytical solutions for linear equations with linear boundary conditions involve eigenvalues, which are to be found by solving non-linear equations. For non-linear equations, one might attempt to get series solution using perturbation or other symbolic techniques, which enable one to solve non-linear equations symbolically with the parameters in the final solution as in analytical solutions. Analytical solutions once derived for the new system can be programmed in a symbolic language like Maple, Mathcad, or Mathematica or FORTRAN, C. A semi-analytical method, which is analytical in one of the independent variables and numerical in the other, is found to be more efficient than both analytical and completely numerical techniques for many problems. The most common numerical techniques for modeling electrochemical systems are the finite difference method, control volume formulation and finite element method. The use of commercially available software such as PDE2D, FLUENT CFD, DASSL, Diffpack, FWEB, GAMS, etc is the trend now in solving mathematical models in electrochemical systems.

### **Extended ECR Technologies**

The novelty in this area are important due to world energy crisis which necessitate combination of electrochemical technology with other technically advanced processes. Here the merger of technology will bridge the gap between various streams of science and technology and also aims to achieve lot of advantages over single technique. These include the combined electrochemical technologies like photoelectrochemical reactors (PECR), bioelectrochemical reactors (BECR) and magnetic field effect.

### *Photoelectrochemical Reactors*

The world energy crisis has stimulated scientists to investigate new routes for finding and testing methods and processes for obtaining renewable and cheap sources of energy. Within this framework, the possibility of solar energy utilization on a large scale must overcome the stage of discovering efficient processes for the photochemical conversion and for the storage. The most promising way for achieving this goal seems the photosplitting of water and related reactions. The methods for obtaining the water photosplitting are essentially based on PECR and on photocatalytic systems (gas-solid and gas-liquid- solid). Extensive research work is currently done all over the world both in universities and in industrial laboratories in these areas [31-32].

Successful commercial application of photochemical reactions requires not only the scientific insight into the photoelectrochemistry of the reactions, but also a rational understanding of the engineering aspects of the photoelectrochemistry process upon which reliable design can be based. An overview of the important engineering problem of the modeling and design of PECR is presented by [33]. Different types of PECR including immersion well, annular, spray-type, fluidised bed, bubble-type, elliptical and film-type are briefly described. The essential model parameters and equations are outlined. The case for systematic design studies is proposed.

The widespread pollution of effluents from industries with various pollutants demands an increase in effort towards the development of technologies for the cleanup of such wastewater. In this field, photoelectrochemical process particularly the heterogeneous photocatalytic (PC) process has attracted considerable attention in recent past. The appeal of this technology is the prospect of complete mineralization of the pollutants into harmless compounds to environment in addition to the abundance and relatively low cost, chemical stability and non-toxic nature of the catalyst. However, the practical application of this technology has been limited due to its low PC efficiency. This high degree of recombination between photogenerated electrons and holes is a major limiting factor controlling the PC efficiency. In this regard, various attempts have been performed to improve the PC activity of photocatalyst [34].

### *Bioelectrochemical Reactors*

In the past 25 years, inorganic fuel cells have been transformed from novelty devices to practical energy transfer-

energy storage units. However, the advantage of the high operating efficiency afforded by these fuel cells is partially offset by (a) the limited viability and high cost of the catalysts, (b) the highly corrosive electrolytes, and (c) the elevated operating temperatures. The possibility exists to reduce some of these problems through the development of bioelectrochemical fuel cells [35]. Such biological/electrochemical systems incorporate either microorganisms or enzymes as an active component within the specified electrode compartments. Recent investigations on the use of cell-free enzyme preparations in the electrode compartments have dealt primarily with developing methodology and defining mechanisms for enhancing the rate of electron transfer from the enzyme-cofactor active site to the solid electrode surface. Applications of this developing technology have been envisioned for analytical chemistry, medical devices, energy transfer, bio-electrochemical synthesis, and detoxification. A membrane-less microbial fuel cell with the internal resistance of 3.9 M $\Omega$  has been shown to generate a stable current of 2 mA within 4 weeks [36] and references there in. They have used the microbial fuel cell for the energy recovery from waste as well as reducing production of excess sludge, disposal of which is very difficult. Thus a membrane-less fuel cell-type ECR was used successfully to enrich electrochemically active microbes that convert organic contaminants to electricity. The theory and problems of bioelectrochemical fuel cells are related to research, both recent and proposed.

Some investigations on the removal of various contaminations using BECR have also been carried out [37]. Simultaneous removal of nitrate and pesticide (copper ion or ammonium nitrogen) was successfully studied by using a BECR. However, the study on the removal of other contaminations is quite limited. In this study, the electrode system was introduced into biofilm reactor and activated sludge reactor. The effect of the electro-chemical reaction on biodegradation of municipal sewage and the effect of electric current on the removal of contaminations were investigated in the biofilm-electrode reactor.

### *Magnetic field effect in ECR*

The magnetic properties of electrolytes and the interactions of externally imposed as well as internally induced magnetic fields on electrolyte properties and ionic transport characteristics has been the subject of steadily increasing interest since Faradaic times. Apart from well-established applications in analytical chemistry, magnetic fields have been shown to exert a theoretically intriguing and practically

important influence on electrolyte behavior on a microscopic and a macroscopic scale. Environmental control, a topic of rapidly expanding importance, is perhaps the newest dominion of application, where much progress can be foreseen in the utilization of magnetically supported force fields. The magnetohydrodynamic theory [38] has been applied extensively in conjunction with convective diffusion theory to the analysis of external magnetic field effects in the hydrodynamic and concentration boundary layer existing at the electrode/electrolyte interface [39]. A logical question to ask upon the field is how magnetic fields can be employed efficiently to improve electrochemical means of environmental protection. Water purification, effluent treatment and corrosion prevention are the most important target areas. Magneto-electrolysis has not yet been shown to be a globally effective method, however, magnetic manipulation i.e., magnetization has been remarkably successful in certain areas of environmental control and holds a definite potential in areas not sufficiently explored so far.

## Conclusion

Only Scott [5] has modeled the electrochemical reactions integrating the mechanistic, kinetic and transport behavior of electrode processes with the hydrodynamic domain of the cell. Pickett [16] has made a critical analysis of electrochemical reactors by means of ChE principles. It is relatively a new endeavor, trying together several scientific and engineering disciplines such as electrochemistry, physical chemistry, hydrodynamics, mass and heat transport phenomena, chemical reaction engineering, mathematical modeling and optimization. The same approach can also be found in White [13] and Fahidy [17]. Thermodynamic provides a framework for describing reaction equilibrium and thermal effects in electrochemical reactors. Rousar [20,21] has made a huge contribution in this regard. Wragg [25] has made a theoretical foundation in predicting concentration-time and current-time behavior of fluidized bed electrochemical reactor systems. He has also concerned with the effects of flow and electrical connection and general strategy on some aspects of the performance of simple electrochemical reactor systems. As observed by Newman [28], the role of transport phenomena, mainly mass transfer, is more important in ECE. The other significant effort towards solving traditional problems associated with ECR and feasibility of ECR system includes Wagner, Tobias, Coeuret, Bockris [3], Hine [4], Trasatti [7], Bard [10].

However much more remains to be done with regard to the industrial electrochemical process design. Dynamic

optimization has been introduced few decades ago to chemical reactors, but it has not been extensively applied to ECR. Also electrochemical process synthesis is largely ignored in the ECE literature despite its importance in ECE practice. The nonlinearity of electrochemical processes manifests as parametric sensitivity, state multiplicity, instability or oscillatory behavior. These features can be predicted by singularity and bifurcation theories, but they have not been widely applied in the field of electrochemical reaction engineering. In flow reactors of various types deviation from ideality can be considerable. Therefore ignoring this factor may lead to gross errors in design. The model will only be as good as the data used. For this purpose, molecular simulations are very important.

The advances that have been made in the use of photoelectrochemical methods particularly for the treatment of contaminated water and air are crucial developments. It holds exiting future opportunities for scientists and engineers from a very wide range of disciplines such as ECE, electrochemistry and photochemistry. The studies on the beneficial effect of electric current on the growth of microbes and their susceptibility to antibiotics are initiated. It aims to improve the growth rate of clinically important microorganism and microbes for organic pollutant control. The sunlight-induced photochemical and combined photochemical-biological degradations of dissolved organic matter play important roles within the global biogeochemical carbon cycle. An idealized mathematical representation of these integrated physicochemical systems is becoming an integral part of all research and development within the field of electrochemical systems.

Models frequently provide more detailed information than experiments. The modeling strategy that may help understanding the mechanisms involved in ECE can be stated as follows: always start by trying the simplest model and then only add complexity to the extent needed or as Einstein said "Keep things as simple as possible, but not simpler". Living in the microchip age has been very useful for treating the subject matter with strong mathematical propensity and arithmetic flavor.

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## Glossary

### *Electrolyte*

Ion conducting medium in an electrochemical cell (e.g. aqueous solutions, molten salts).

### *Electrode*

Electron conducting material in contact with the electrolyte with an electrochemical reaction taking place at the interface.

### *Anode*

The electrode at which oxidation takes place (a process by which electrons are released). The anode is the positive pole in an electrolytic cell (the polarity is reversed in a spontaneous electrochemical process).

### *Cathode*

The electrode at which reduction takes place (a process by which electrons are taken up). The cathode is the negative pole in an electrolytic cell (the polarity is reversed in a spontaneous electrochemical process).

### *Electrochemical cell*

At least two electrodes, an anode and a cathode, combined with an electrolyte. If both electrodes are placed in the same solution, the cell is undivided. If the electrodes are in different electrolyte chambers separated by a diaphragm or membrane, the cell is known as a divided cell.

### *Current efficiency*

Actual mass of product obtained related to the mass of product determined theoretically according to Faraday's law.

### *Space-time yield*

Mass of product obtained per unit time and cell volume.

### *Residence time*

The time required for any small volume element of the electrolyte to pass through the cell once.

### *Scale-up*

Increase in scale of a chemical or electrochemical reactor (cell) in order to achieve a higher throughput, with due consideration to the process and reaction engineering relationships.

### *Product yield*

Actual mass of product obtained related to the mass of product predicted by stoichiometric calculations.

### *Specific energy consumption*

The amount of energy required to produce 1 kg product.

### *Energy yield*

The energy required thermodynamically to produce a certain mass of product related to the actual energy consumed.

## References

1. D. Pletcher and F.C Walsh, "Industrial Electrochemistry", Chapman and Hall, London, (1990)
2. C. L. Mantell, "Electrochemical Engineering", McGraw-Hill, New York, (1960)
3. J. O'. M. Bockris and A. K. N. Reddy, "Modern Electrochemistry 2B : Electrodics in Chemistry, Engineering, Biology and Environmental Science", Plenum, US, (2001)
4. F. Hine, "Electrochemical Processes and Electrochemical Engineering", Plenum, US, (1985)
5. K. Scott, "Electrochemical Reaction Engineering", Academic Press, London, (1991)
6. K. J. Vetter, "Electrochemical Kinetics", Academic Press, UK, (1967)
7. S. Trasatti, "The Absolute Electrode Potential: An Explanatory Note" *J. Electroanal. Chem. Interfacial Electrochem.* 209, 417 (1986); "The Absolute Electrode Potential – The End of the Story" *Electrochim. Acta* 35, 269 (1991)
8. G. Prentice, "Electrochemical Engineering Principles", Prentice Hall - Englewood Cliffs, New Jersey, (1991).
9. E. Heitz and G. Kreysa, "Principles of Electrochemical Engineering", VCH, Germany, (1986)
10. A. J. Bard and I Rubinstein, "Electroanalytical Chemistry: A Series of Advances (Electroanalytical Chemistry)", Vol. I-XII, Marcel Dekker, NY, (2003)
11. K. Scott, "Electrochemical Process for Clean Technology", The Royal Society of Chemistry, Cambridge, (1995)
12. R. C. Alkire, R. Beck and D. Varjian, "Electrochemical Process and Plant Design (Proceedings volume 83-6)", Electrochemical Society, USA, (1983)
13. R. E. White, R. F. Savinell and A. Schneider, "Electrochemical Engineering Applications (AIChE Symposium Series ; No 254 V 83)", AIChE, USA, (1987)
14. B. Vijayasekaran and C. Ahmed Basha, *Bull. Electrochem.*, 20 (2004) 133
15. R. F. Savinell, J. M Fenton, A. C. West and Scanlon, "Tutorials in Electrochemical Engineering-Mathematical Modeling: Proceedings of the International Symposium

- (Proceedings (Electrochemical Society), V. 99-14.)”, Electrochemical Society, USA, (1999)
16. D. J. Pickett, “Electrochemical Reactor Design”, Elsevier Publishing Company, Amsterdam – The Netherlands, (1979)
  17. T. Z. Fahidy, “Principles of Electrochemical Reactor Analysis”, Elsevier Publishing Company, New York, (1985)
  18. D.E. Goldberg, “Genetic Algorithms in Search, Optimization and Machine Learning”, Pearson Education, New Delhi (2002)
  19. B. Vijayasekaran, C. Ahmed Basha and N. Balasubramanian, *Chem. Biochem. Engg. Q.*, 18 (2004) 359
  20. I. Rousar, K. Micka and A. Kimla, “Electrochemical Engineering I (Part A-C)”, Elsevier Publishing Company, New York, (1986)
  21. I. Rousar, K. Micka and A. Kimla, “Electrochemical Engineering II (Part D-F)”, Elsevier Publishing Company, New York, (1986)
  22. H. Wendt and G. Kreysa, “Electrochemical Engineering: Science and Technology in Chemical and Other Industries”, Springer-Verlag, US, (1998)
  23. O. Levenspiel, “Chemical Reaction Engineering”, John Wiley & Sons, New York, (1998)
  24. F. Goodridge and K. Scott, “Electrochemical Process Engineering – A guide to the design of electrolytic plant”, Plenum Publishing Corporation, New York, (1995)
  25. F. Lapique, A. Storck and A. A. Wragg, “Electrochemical Engineering and Energy (The Language of Science)”, Plenum, US, (1995)
  26. X.G. Zhou, X.S. Zhang, X. Wang, Y.C. Dai and W.K. Yuan, *Chem. Eng. Sci.* 56 (2001) 1485
  27. K. Jayaraman and C. Ahmed Basha, “Electroorganic Synthesis Engineering”, in L.K. Doraiswamy, “Organic Synthesis Engineering”, Oxford University Press, London, Ch 21, (2001) 682
  28. J. Newman, “Electrochemical Systems”, Prentice Hall - Englewood Cliffs, New Jersey (1991)
  29. De La Rue, R. E. White and Tobias, *J. Electrochem. Soc.*, 106 (1959) 827
  30. A. C. West, “Effects of Nonuniform Potential and Current Distribution in Electrochemical Systems”, Ph.D. Thesis, University of California, Berkeley, (1989)
  31. P. Pichat, “Photochemical conversion and storage of solar energy”, Kluwer Academic Publishers, Dordrecht, (1991)
  32. H. Al-Ekabi, D.E. Ollis, “Photocatalytic purification and treatment for water and air”, Elsevier, Amsterdam, (1993)
  33. K. Rajeshwar and J.G. Ibanez, “Environmental Electrochemistry”, Academic Press, London, (1997)
  34. N. Serpone, E. Pellizzetti, “Photocatalysis: Fundamentals and applications”, Wiley-Interscience, Amsterdam, (1989)
  35. A.K. Shukla, P. Suresh, S. Berchmans and A. Rajendran, *Current Science*, 87 (2004) 455
  36. J.K. Jang, T.H. Pham, I.S. Chang, K.H. Kang, H. Moon, K.S. Cho, B.H. Kim, *Process Biochemistry*, 39 (2004) 1007
  37. A.J. Bard, M. Stratmann. G.S. Wilson, (Eds) “Bioelectrochemistry”, Wiley-VCH, Germany, (2002)
  38. J.A. Shercliff, “A Textbook of Magnetohydrodynamics”, Pergamon Press, Oxford, (1965)
  39. T. Z. Fahidy, *J. Appln. Electrochem*, 13 (1983) 553