

Electrochemical Reaction Engineering



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ELECTROCHEMICAL REACTION ENGINEERING

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ELECTROCHEMICAL REACTION ENGINEERING

*To my wife, Jean, and my children
Tamsin and Alexander and
Amy and Sophie (who were born in
spite of the preparation of this book)*

Preface

A vital element in any chemical manufacturing process is the reactor. This unit at the heart of the process (perhaps the correct analogy should be the stomach), where chemical change as well as physical change occur, requires a culmination of the principles of physics, chemistry and mechanics in its design and construction as well as the principles of economics.

In non-electrolytic process industries the art of the design, construction and operation of this unit is well developed. New synthesis routes can be engineered from sound design principles established in an ever expanding and developing field. The same, unfortunately, cannot be said of electrosynthesis in which reactor design methods and strategies are not well documented and are lagging behind more traditional reaction routes.

This situation should not and indeed, need not, arise if the electrochemical technologist or electrochemist were aware of the principles of chemical and catalytic reaction engineering and the analogy between the electrochemical "cell" and catalytic reactor. The intrusion of that fickle reagent, the electron, would seem to often obscure the chemical or process engineer's view of electrochemical reactor design. The requirements for any design within the development of a commercial process are the same. The procurement of chemical and physical data is essential and in particular information of the conversion rates of desired and undesired products and the interrelation with specific operating parameters must be known. The culmination of this knowledge into a physicochemical model would allow predictions of reactor performance to be made and lead eventually to a design methodology or strategy. By this means questions such as what reactor type is appropriate, what mode of operation(s) is to be used and what size of reactor is required can be answered. Within an overall process engineering framework, a final decision as to the most suitable synthesis route must also be made. However, the answer to a question of this magnitude is outside the scope of this book or any one book.

The objective of this book is to describe reactor design methods appropriate to the electrochemical process industries and to try to bridge the gap between the electrochemist and the chemical engineer in such a design task. It is not the intention of this text to describe the wide range of industrial electrochemical processes nor to give detailed descriptions of current processes and operating conditions. The book deals with the engineering of electrochemical reactors and not the technology, although where appropriate details of industrial syntheses will be cited to illustrate design methodology.

It will be quickly seen that the main impetus behind the work is the treatment of multiple reactions coupled with the physical phenomena of adsorption and mass transfer. To prepare the reader for this the first two chapters will deal with more fundamental material. Early on in these chapters the reader is introduced to some basic aspects of chemical reaction engineering and thermodynamics. This should enable the general treatment to start on a sound footing and later be of benefit in the analysis of coupled chemical and electrochemical reactions.

Chapter 1 effectively defines various parameters which will allow reactor performance to be characterized and considers such factors as the thermodynamics and reaction kinetics of simple electrode processes. The relationship between reaction rate and mass transport is also considered. Reactor types are classified as a precursor to Chapter 2 where the electrochemical reaction engineering of single electrode reactions is considered. Here, various modes of reactor operation are analysed. Chapter 3 deals with the kinetics of electrode processes in greater depth introducing the effects of adsorption, electrocatalysis and the influence of chemical reaction. Experimental methods for the evaluation of complex reaction mechanisms are outlined.

Chapter 4 builds on Chapter 3 and looks in detail at the design methods for ideal reactors operating both potentiostatically and galvanostatically. A significant part of this chapter is devoted to reactions which couple both electrochemical and chemical processes. The performance of such reactors is distinguished in terms of consecutive and concurrent mass transport effects.

Chapter 5 considers aspects of non-ideal flow and their relationship to electrochemical reactor design. An integral part of this chapter will be the dynamic response of electrochemical reactors. Chapter 6 deals with design methods for paired synthesis reactions and undivided cells and covers aspects of two phase reactor design and ionic transport by migration.

The problem of reaction rate or current distribution in electrochemical reactions is introduced in Chapter 7 and the significance of the problem is dealt with in relation to both two and three dimensional electrodes. Finally, Chapter 8 deals with important design factors such as thermal characteristics, energy and voltage balances and non-isothermal operation. The reader is introduced to process design and optimization and the more "practical" aspects of electrochemical hardware.

In writing this book I have been encouraged by a number of colleagues for the need for a concisely written treatment of reaction engineering dealing with aspects of relatively complex electrochemistry. The treatment clearly deals with only a small area of process engineering but should go some way in filling a void in the field of reaction engineering.

K. Scott

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The seed for this book was planted in 1985 by Professor F. Goodridge who first tempted me into the area of electrochemical engineering in the early 1970's and who I now sincerely thank.

During this period my efforts were guided by two other members of Newcastle-upon-Tyne University, Drs R.E. Plimley and A.R. Wright, and I thank them for that contribution.

I am indebted to the staff at Teesside Polytechnic who have encouraged and helped me in many ways in my endeavours to produce this book and in particular Dr I.F. McConvey (now at ICI C and P) for our many discussions and subsequent friendship.

NOTATION

A	magnitude of step change
a, b	order of reaction for component A, B
a, b	Tafel coefficients
a_j	activity of component j
C	capital cost
C_j	concentration of species j
C_f	friction factor
C_F	independent costs
C_I	investment cost
C_K	product cost
C_P	production cost
C_S	sale value
$C.E.$	current efficiency
C_j^s	concentration of species j at the surface
C_{jo}	initial concentration of species j
C_{ji}	inlet concentration of species j or intersacial species
C_p	heat capacity
d	interelectrode distance
d_v	vessel diameter
d_p	mean particle diameter
d_i	impeller diameter
d_l	characteristic dimension
D_e	dispersion coefficient
D_j	diffusivity of species j
D_a	Damköhler number
$\bar{D}a \left\{ \begin{array}{l} \bar{D}r \end{array} \right\}$	sum of diffusion and dispersion coefficients radially or axially
e	voidage
emf	electromotive force
E	electrode potential
E_T	cell voltage
E_A	enhancement factor
E_{Ax}	enhancement factor for instantaneous reaction
E_e	equilibrium potential
E_o	open circuit voltage
E^o	standard reversible potential
E^+	anode potential
E^-	cathode potential
E_{min}	minimum cell potential
E_{IR}	ohmic voltage loss
f	parameter (F/RT)
F	Faraday
G	Gibbs free energy
G_{is}	transfer function
ΔG	Gibbs free energy change

NOTATION

ΔG°	standard Gibbs free energy change
ΔG_{ads}	free energy change of adsorption
g	constant characterizing potential dependence of Temkin isotherm
f_g	volume fraction of gas
G_j	transfer function
h	hydrostatic head
h_k	heat transfer coefficient
H	enthalpy
$H(t - \lambda)$	Heaviside shifting function
ΔH_r	heat of reaction
i	current density
i	interest rate
i_L	limiting current density
i^*	dimensionless current density = $i_1/n_1 F k_{LA} c_{Ao}$
i^+	dimensionless current density = $i/(n_1 F C_{Ao} k_1)$
\bar{i}_j	partial current density for step j in forward direction
\tilde{i}_j	partial current density for step j in reverse direction
i_o	exchange current density
I	current
I_j	partial current for reaction j
I_{jL}	limiting current of step j
k	homogeneous reaction rate constant
k_a, k_b	adsorption rate constants
k_{-a}, k_{-b}	desorption rate constants
k_{f_1}	forward electrochemical rate constant
k_j	electrochemical rate constant in forward direction for step j
k_{-j}	electrochemical rate constant in reverse direction for step j
K_e	electrochemical equilibrium parameter = k_{f_1}/k_{b_1}
K_j	electrochemical or adsorption equilibrium constant for step j
k_s	reaction rate constant of surface reactions
k_{sh}	standard rate constant relative to hydrogen electrode
k_{b_1}	reverse electrochemical rate parameter
k_{Lj}	mass transport coefficient of species j
k_{j1}	forward electrochemical rate parameter
K	equilibrium constant
K_p	gain
K_a	equilibrium constant for adsorption
K_w	equilibrium constant for the formation of water
l_i	thickness of insulation
l_p	wall thickness
L	electrode length
m_1, m_2	orders of electrochemical reaction
m	total mass
m	distribution coefficient
m_j	mass of components j
M	molar ratio of initial or inlet concentrations
M_j	molar mass of component j
n	number of steps in a series reaction
n	amortization period

n	overall order of reaction
n	surface reaction molecularity
n_e	number of electrochemical steps in a series reaction
N	number of tanks
\bar{N}_j	flux of species j
n_j	number of electrons in reaction j
N_j	mol of species j
n_i	rotational speed
N	theoretical number of plates
p, q	order of reaction
p	diaphragm permeability
P	pressure
F_a	annual profit
P_j	partial pressure of component j
Q	heat flow
Q_g	volumetric flowrate of gas
r	recycle ratio
r	radial dimension
r_i	rate of electrode processes
r_{-i}	rate of electrode processes in reverse direction
R	gas constant
R	reflux ratio
R_e	internal electrical resistance
R_j	reaction rate per unit volume
R_{js}	reaction rate per unit area
ROI	return on investment
s	Laplace transform operator
S	sales value
S	surface area
S	selectivity
ΔS	entropy change
t	time
t_p	payback time
t	transport number
t	diaphragm or membrane thickness
T	temperature
T_i	inlet temperature of electrolyte
t_c	recirculation time
t_j	transport number
T_c	impeller coefficient
θ_j	surface coverage of species j
u	velocity
u_r	peripheral velocity
U	internal energy
U	overall heat transfer coefficient
v	volumetric flowrate of electrolyte
v	potential sweep rate
V	volume
V_g	molar volume of gas
W	work

NOTATION

W	electrode width
w	angular velocity
W_1, W_2, W_j	reaction order exponents
x	dimension of reactor
x_j	mol fraction of species j
x_{je}	equilibrium conversion
y	co-ordinate direction
X_1, X_2	perturbation variables
X_j	fractional conversion of species j
X_{jD}	fractional conversion when the limiting current is reached
Y_i	instantaneous yield
Y_j	overall material yield of species j
Y_o	operational yield
z	dimension of reactor
z	valency
S.T.Y.	Space Time Yield

Dimensionless Number

Bo	Bodenstein number
Pr	Prandtl number
Gr	Grashoff number
ϕ	dimensionless voltage drop in the diaphragm
Ha	Hatta number
Hi	Hinterland ratio
Nu	Nusselt number
N_H	Hine number
N_M	McMullin number
Pe	Peclet number
Re	Reynolds number
Sc	Schmidt number
Wa	Wagner number
$E(t)$	exit age distribution function

Greek

α	constant describing the potential dependency of the reaction rate
α_j	relative velocity
α_1	specific investment cost
α_2	electricity costs
β	constant describing the potential dependency of the reaction rate
γ	number of steps preceeding r.d.s.
γ	latent heat of vapourisation
δ	diffusion film thickness
ϵ	fractional expansion factor
ϵ	emmissivity
ϵ_r	rectifier conversion efficiency
ϵ_v	voltage efficiency
κ	conductivity of electrolyte

κ_s	effective conductivity of solution
κ_g	conductivity of electrolyte with gas fraction f_g
κ_m	effective conductivity of metal phase
κ_j	effective conductivity of electron exchange
η	interphase effectiveness factor
η	overpotential
σ	Stefan Boltzman constant
σ	specific surface area of the electrode
σ_l^2	variance
σ_θ^2	dimensionless variance
ν_j	stoichiometric coefficient of species j
ξ_j	degree of conversion of species j
γ_T	total number or concentration of active sites
γ_v	number or concentration of vacant sites
γ_c	dimensionless time
ρ	fluid density
μ	kinematic fluid viscosity
μ	reaction layer thickness
ν	equal to group ($\sigma \times \tau$)
ν	dynamic fluid viscosity
$\Delta\Phi_j$	net input of j into the system
τ	residence time or holding time
τ_g	dimensionless residence time = $\sigma i_T \tau / n_1 F C_{Ai}$
τ_r	dimensionless time = $\sigma(k_{f1} + k_{b1})t$
τ_R	residence time under recycle conditions
τ_L	dimensionless time for mass transport controlled reactions
ϕ	potential
ϕ	effectiveness
$\Delta\phi$	dimensionless voltage drop in the diaphragm
ϕ	dimensionless group = $\sqrt{(kD_j/k)}$
$\bar{\gamma}$	number of steps preceeding the rate determining step
$\bar{\gamma}$	number of steps after the rate determining step
$\bar{\tau}$	dimensionless time in dispersed plug flow model = (ut/L)

Subscripts

ads	adsorbed species
a	anode
c	cathode
g	gas phase
i	inlet condition
j	species or component
e	equilibrium
fs	formation
i	ion species
i	instantaneous
i	step i
j	species
mf	minimum fluidization

NOTATION

<i>min</i>	minimum value
<i>n</i>	number of the reactor
<i>o</i>	initial amount or condition
<i>o</i>	overall
<i>p</i>	product
<i>R</i>	recycle condition
<i>s</i>	surface
<i>s</i>	transformed variable
<i>cs</i>	combustion
<i>T</i>	total
P.F.R.	plug flow reaction
D.P.F.R.	dispersed plug flow reaction

Superscripts

<i>o</i>	standard state
<i>s</i>	surface concentration
+	steady-state quantity in defining perturbation variables

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