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Modelling of tank electrolysers via Markov chains

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The establishment of CSTER–perfect mixer networks via the theory of Markov chains for non-ideal tank electrolysers is described. Such networks, matched to tank electrolysers via experimental exit-age distribution data, can serve (as equivalent models) for the analysis of electrolyser behaviour.

Nomenclature

A	electrode area
c	electrolyte concentration; c_{i} same for inlet conditions; c_1 same for exit conditions
E	exit age
k_{M}	mean mass transport coefficient
P	transition probability matrix with elements p_{ij}
Q	volumetric flow rate of the electrolyte
t	time
V	effective electrolyser volume
$X(t)$	time-dependent random process
α	recycle ratio
β	lumped parameter, equal to $k_{\mathrm{m}}A/Q$
ε	symbol denoting the state of a Markov chain
θ	dimensionless time, equal to Qt/V

1. Introduction

In the analysis of tank electrolysers the CSTER (continuous-flow stirred-tank electrolytic reactor) concept has been used widely, e.g. [1–3], due to the relatively simple mathematical structure of its governing (balance) equations. The approach, based on the perfect agitation postulate, cannot adequately describe the behaviour of a tank electrolyser with appreciable concentration and/or temperature gradients; one treatment of this problem in terms of a specific technique of stochastic system dynamics has recently been proposed [4]. An alternative approach to non-ideal tank electrolyser analysis can be made via experimental exit-age distribution studies where the behaviour of a real electrolyser is approximated – as closely as required – by an appropriate 'equivalent' network of CSTERs and ideal mixers. The Markov chain formulation can be chosen conveniently as the mathematical framework, inasmuch as associated finite difference equations are easily established on the basis of linear algebra and they can be quickly implemented on a relatively simple computing device (e.g. a programmable calculator). The usefulness of the Markov chain concept has been recently demonstrated in the analysis of flow systems and chemical reactors [5–8]; the purpose of this paper is to explore the scope and the attractiveness of this technique in electrochemical engineering where practical applications of probability theory are still scarce.

2. Theory

Following the basic theory of Markov chains, summarized in Appendix A, the transitional probabilities (i.e. the elements of the transitional probability matrix P) in a CSTER operating under mass transport control can be expressed as follows.
Flow

$$\frac{Q}{V}\Delta t$$

Electrochemical reaction occurring at the limiting current

$$\frac{k_M A}{V}\Delta t$$

No change in the CSTER

$$1 - \frac{Q\Delta t}{V} - \frac{k_M A}{V}\Delta t$$

These probabilities are the 'building blocks' of P in the following manner. Let m be the state at an arbitrary time interval and $(m + 1)$ the state past an arbitrarily small Δt time interval. Then, p_{11} is the matrix element pertaining to no change for an entering electrolyte element, p_{12} is the matrix element pertaining to the electrode reaction, p_{13} is the matrix element pertaining to bypass of an entering element to the exit (or absorbing) state and so forth; these matrix elements are independent of state m. Thus, the transition probability matrix is

$$P = \begin{pmatrix} 1 - \frac{Q\Delta t}{V} - \frac{k_M A\Delta t}{V} & \frac{k_M A\Delta t}{V} & \frac{Q\Delta t}{V} \\ 0 & 1 - \frac{k_M A\Delta t}{V} & \frac{k_M A\Delta t}{V} \\ 0 & 0 & 1 \end{pmatrix} \tag{1}$$

where the zero elements denote the lack of recycling and the irreversibility of flow and reaction conditions. Replacing the exit concentration–time derivative in the substance balance

$$\frac{dc_l}{dt} = \frac{Q}{V}c_i - \frac{Q}{V}c_l - \frac{k_M A}{V}c_l$$

by the forward-difference approximation

$$\frac{dc_l}{dt} \simeq \frac{c_l(m+1) - c_l(m)}{\Delta t}$$

the iteration formula

$$\begin{aligned} c_l(m+1) &= c_l(m)\left(1 - \frac{Q\Delta t}{V} - \frac{k_M A\Delta t}{V}\right) + \frac{Q\Delta t}{V}c_i \\ &= x_i(m+1) + c_l(m)p_{11} \end{aligned} \tag{2}$$

is obtained. If c_i remains constant, then

$$x_i(m+1) = x_i = \frac{Q\Delta t}{V}c_i = \text{constant}$$

The accuracy of Equation 2 depends on the size of Δt; in a numerical implementation the maximum value of Δt acceptable for a predetermined decimal accuracy can be quickly established by a systematic reduction procedure, as shown in Appendix B, where the results of numerical computation via Markov chain modelling are compared with the analytical solution of the CSTER equation.

In applying this framework to the modelling of non-ideal tank electrolysers, the real electrolyser is replaced by a CSTER–perfect mixer network whose theoretical exit-age distribution matches closely (i.e. within a predetermined numerical accuracy) the exit-age distribution determined experimentally. If n is the position of the last element in the network, adjacent to exit (or absorbing) state with identifying index $(n + 1)$, the exit age distribution in the absence of recycle flow into the nth element is given by Equation 3:

$$E(m)\,\Delta t \;=\; p_{\mathrm{n}}(m)\,p_{n,n+1} \tag{3}$$

which is the probability that an electrolyte element will leave the electrolyser in the $(m,\ m + 1)$ time interval, provided it entered the electrolyser at time instant $m = 0$. If time is normalized with respect to the apparent mean residence time, $\bar{t} = V/Q$, the Markov chain analysis can be carried out in terms of fractional time $\theta = Qt/V$ where $\Delta\theta$ replaces Δt and the elements of P are modified accordingly. In the sequel, two specific networks will be analysed in detail, although any network with arbitrarily positioned CSTER and perfect mixer building blocks can, in principle, be constructed.

3. Model A: a two-element CSTER cascade with recycle

As shown by the block diagram in Fig. 1, two CSTERs are in series in the forward loop, and a perfect mixer in the feedback loop indicates electrolyte recycling; they are indexed 1 to 3, respectively, and the exit or absorbing state has index 4. The model parameters are the recycle ratio α, the lumped dimensionless mass-transport parameter $\beta = k_{\mathrm{M}}A/Q$, and $\Delta\theta$ is the dimensionless time

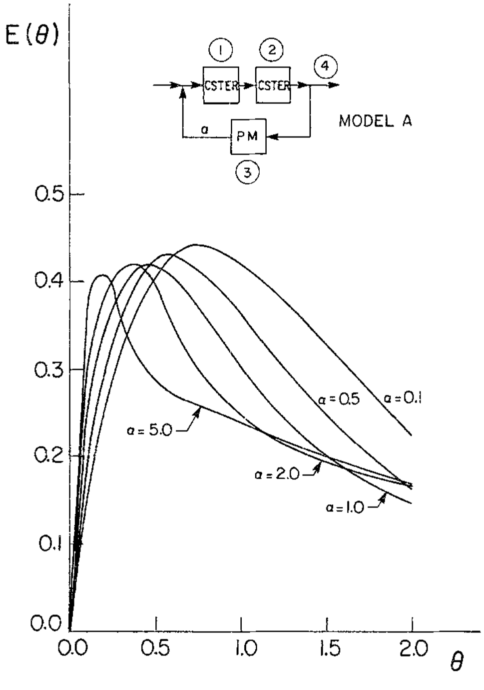

Fig. 1. Exit-age distribution curves via model A, as a function of the recycle ratio α (the numerical parameters are given in Appendix B). $\Delta\theta = 0.02$ ($\Delta t = 1$ min).

interval for transition. The transitional probability matrix

$$P = \begin{pmatrix} 1 - \Delta\theta\,(1 + \alpha + \beta) & \Delta\theta\,(1 + \alpha + \beta) & 0 & 0 \\ 0 & 1 - \Delta\theta\,(1 + \alpha) & \alpha\Delta\theta & \Delta\theta \\ \alpha\Delta\theta & 0 & 1 - \alpha\Delta\theta & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \tag{4}$$

contains time–invariant elements, independent of m. Consequently, the state probabilities are computed via the scheme

$$p_1(m + 1) = p_{11}p_1(m) + p_{31}p_3(m) \tag{5a}$$

$$p_2(m + 1) = p_{12}p_1(m) + p_{22}p_2(m) \tag{5b}$$

$$p_3(m + 1) = p_{23}p_2(m) + p_{33}p_3(m) \tag{5c}$$

and the exit–age distribution is given by the formula

$$E(m) = p_2(m) \tag{6}$$

in terms of the dimensionless time $\theta = m\Delta\theta$.

4. Model B: mixer–CSTER–mixer cascade with recycle

In this configuration a CSTER is embedded between two perfect mixers in the forward loop and, as in model A, electrolyte recycling is represented by a perfect mixer in the feedback loop (Fig. 2). As in the case of model A, the system is fully described in terms of the α and β parameters and $\Delta\theta$.

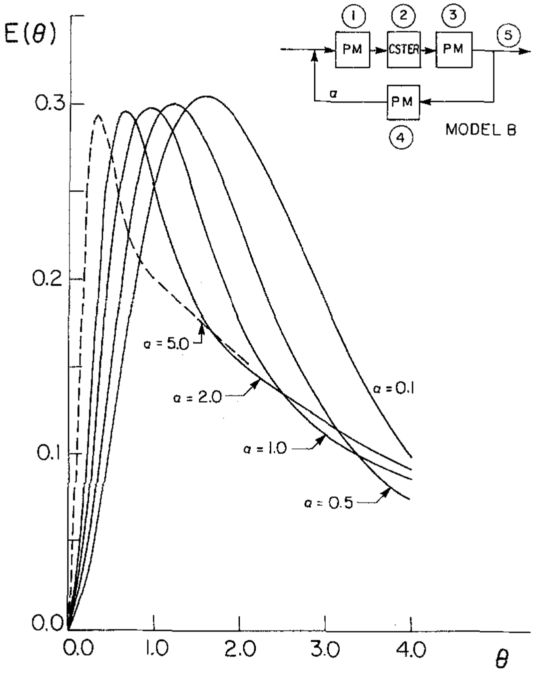

Fig 2. Exit-age distribution curves via model B, as a function of the recycle ratio α (the numerical parameters are given in Appendix B). $\Delta\theta = 0.02$ ($\Delta t = 1$ min).

The transitional probability matrix is given by

$$P = \begin{pmatrix} 1 - \Delta\theta\,(1 + \alpha) & \Delta\theta\,(1 + \alpha) & 0 & 0 & 0 \\ 0 & 1 - \Delta\theta\,(1 + \alpha + \beta) & \Delta\theta\,(1 + \alpha + \beta) & 0 & 0 \\ 0 & 0 & 1 - \Delta\theta\,(1 + \alpha) & \alpha\Delta\theta & \Delta\theta \\ \alpha\Delta\theta & 0 & 0 & 1 - \alpha\Delta\theta & 0 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix} \tag{7}$$

and the state probabilities are computed as

$$p_1(m + 1) = p_{11}p_1(m) + p_{41}p_4(m) \tag{8a}$$

$$p_2(m + 1) = p_{12}p_1(m) + p_{22}p_2(m) \tag{8b}$$

$$p_3(m + 1) = p_{23}p_2(m) + p_{33}p_3(m) \tag{8c}$$

$$p_4(m + 1) = p_{34}p_3(m) + p_{44}p_4(m) \tag{8d}$$

with exit-age distribution

$$E(m) = p_3(m) \tag{9}$$

5. Discussion: application to the modelling of non-ideal tank electrolysers

The typical exit-age distribution curves shown in Figs 1 and 2 indicate that the shape of the E curves and their maxima are a sensitive function of time; therefore, the curves are well suited for experiment-based identification. In so doing, the experimental exit–age distribution of an electrolyser is compared to theoretical E curves; the experimental technique has been described in detail in the literature (e.g. [9, 10]). As an illustration, the experimental E distribution of a hypothetical electrolyser given in Table I compares closely with the $\alpha = 1$/model B curve in Fig. 2 with an error variance of 2.76×10^{-4}; thus the behaviour of the electrolyser can be closely approximated by a configuration of mixer–CSTER–mixer–cascade with recycle, where the recycle ratio is unity. In further analysis of the electrolyser the linear analytical equations pertinent to this configuration can be employed as a replacement for non-ideality. Complications may, however, arise if the experimental exit-age distribution possesses comparable variances with respect to a number of different model-oriented E curves; model discrimination methods, e.g. the maximum likelihood principle [11, 12] may serve for selecting the statistically 'best' model.

Table 1. Experimental exit-age distribution in a hypothetical tank electrolyser for illustration

θ	$E(\theta)$
0.10	0.0167
0.20	0.0628
0.30	0.1192
0.40	0.1585
0.50	0.2724
0.60	0.2431
0.70	0.2813
1.00	0.3134
1.20	0.2693
1.50	0.2391

An alternative to the Markov chain approach, i.e. compartmental modelling based on continuous time, would treat the electrolyser as a continuous Markov chain via a stochastic differential equation (Kolmogorov equation) yielding the probability density function of random lifetime for the flow elements, its expectation and variance, etc. Since numerical improvements over the mathematically less cumbersome discrete Markov chain approach in other areas of stochastic flow reactor modelling [13] are modest, except in the case of very low mean residence times, the continuous-time alternative does not offer particular advantages for manipulative efficiency.

Extension to sublimiting current conditions requires the inclusion of the fractional concentration factor $\gamma(1)$ or $\lambda(3)$ relating exit electrolyte concentration to surface electrolyte concentration: the numerical value of this factor is to be computed from an appropriate voltage balance if the imposed potential drop between anode and cathode is known.

In conclusion, the Markov chain-based approach may serve as a viable means of treating non-ideal tank electrolyser behaviour, especially when spectral analysis required by a previously proposed alternative [4] is judged unattractive. Stochastic techniques may prove, in general, useful in the modelling of electrochemical systems, and research with this purpose in mind is well warranted.

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Appendix A. Summary of Markov chain theory

The concept of Markov chains has been widely used in various scientific areas, and many comprehensive texts (e.g. [14–18]) are available for its study; this summary is based on a concise treatment by Rozanov [19].

Let a physical system be characterized by states ε_1, ε_2 and so on, any one of which is attainable randomly at discrete times (or continuously, in the case of continuous Markov chains), starting from some initial time $t = 0$. The following probabilities can be defined for a random variable $X(t)$:

$$\text{(i)} \quad p_i^0 = P[X(0) = \varepsilon_i]; \quad i = 1, 2, \ldots \tag{A1}$$

is the probability that at zero time the system occupies state ε_i

$$\text{(ii)} \quad p_{ij} = P[X(m+1) = \varepsilon_j[X(m) = \varepsilon_i]; \quad i,j = 1, 2, \ldots \tag{A2}$$

is the probability that the system occupies state ε_j at the $(m + 1)$th time instant, given that the state occupied at the mth time instant was ε_i. The transition probabilities p_{ij} do *not* depend on m.

$$\text{(iii)} \quad p_j(m) = P[X(m) = \varepsilon_j]; \quad j = 1, 2, \ldots \tag{A3}$$

is the probability that the system will be in state ε_j after m steps. Then, by the theorems of conditional probability,

$$p_{ij}(m) = \sum_k p_{ik}(m-1)p_{kj}; \quad m = 1, 2, \ldots \tag{A4}$$

or, alternatively,

$$P_j(m) = \sum_k P_k(m-1)P_{kj}; \quad m = 1, 2, \ldots$$

where

$$p_{ij}(0) = \left| \begin{array}{ll} 1; & i = j \\ 0; & i \neq j \end{array} \right. \tag{A5}$$

the latter relationship indicating the initial state of the chain. In terms of the transitional probability matrix, $P = \{p_{ij}\}$, the alternative representation of the chain is the vector matrix form

$$p(m) = P(0)\,P^m \tag{A6}$$

where $P^m = P(m)$ due to the rules of matrix multiplication.

In the case of a reactor, the history of a molecule or particle, (called an element), can be described via transitional probabilities related to flow and chemical reaction, e.g. $p_{ii}(m)$ is the probability that the element has not flown out of the system and has not undergone reaction at time instant m [8]. A distinct probability to each physical change can be ascribed so that every element in P is made up of such probabilities. The matrix element positions correspond to physical locations of transition: if, for example, index 1 denotes the reactor and index 2 denotes exit (known also as absorbing state, captor state, death state in various areas of application) the P matrix element, $p_{12}(m)$, is the probability that at time instant m a physical element has exited while it was in the reactor at time instant $m - 1$. Conversely, $p_{21}(m)$ is the probability that at time instant m the physical element is in the reactor while it was in the exit stream at time instant $m = 1$; of course, $p_{21} = 0$, if there is no recycling or backmixing. In a perfectly mixed container the transitional probability of outflow over a period Δt is $Q\Delta t/V$; the smaller the value of Δt the better the Markov chain approximation to a continuous time-flow process.

Appendix B. Numerical illustration for a CSTER

The CSTER with a single electrode reaction at each electrode, but considering only one electrode process of importance, can be described by three states: (i) the reactant state, (ii) the product (e.g. electrode deposit) state, and (iii) the exit or absorbing state. There is no recycling or backmixing; the inflow electrolyte concentration is c_i, and at zero time the concentration in the CSTER is zero (arbitrary choice). The CSTER is operated at limiting current conditions. The transitional probability matrix is given by Equation 1; assuming $c_i = 0.04\,\mathrm{mol\,l^{-1}}$, $Q = 2\,\mathrm{l\,min^{-1}}$, $A = 0.956\,\mathrm{m^2}$, $V = 100\,\mathrm{l}$, $k_M = 1.68 \times 10^{-3}\,\mathrm{cm\,s^{-1}}$, the exit electrolyte concentration equation (Equation 2) varies with Δt as shown in Table B1.

Table B1. Variation of c_l (m + 1) *with* Δt

Δt *(min)*	c_l (m + *1*)
10.0	$8 \times 10^{-3} + 0.70364 c_l(m)$
5.0	$4 \times 10^{-3} + 0.85182 c_l(m)$
2.5	$2 \times 10^{-3} + 0.92591 c_l(m)$
1.0	$8 \times 10^{-4} + 0.97036 c_l(m)$

Table B2. The effect of Δt *on solution accuracy*

m	Δt = *2.5 min*			Δt = *1.0 min*		
	t (min)	*10^3 c_l (mol l^{-1})*		*t (min)*	*10^3 c_l (mol l^{-1})*	
		Markov chain	*Analytical*		*Markov chain*	*Analytical*
0	2.5	2.0	1.928	1	0.8	0.7884
1	5.0	3.713	3.718	2	1.576	1.554
2	7.5	5.438	5.381	3	2.329	2.297
3	10.0	6.982	6.924	4	3.060	3.017
4	12.5	8.465	8.358	5	3.770	3.718

The analytical solution

$$c_1(t) = 0.026994\,[1 - \exp(-0.02964t)]$$

agrees closely with the Markov chain solutions at $\Delta t \leqslant 1$ min as shown in Table B2 (in this example Δt must be rather small since the zero initial condition on c_1 implies a discontinuity for a discrete numerical solution at very small physical times).

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