JOURNAL OF APPLIED ELECTROCHEMISTRY **28** (1998) 411–416

An application of queuing theory to the dynamics of anodic dissolution

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Received 29 November 1996; revised 10 April 1997

Queuing theory is applied to oscillatory phenomena encountered during anodic dissolution, with numerical illustration provided by a laboratory-scale copper dissolution process. The theory interprets oscillation as a two-phase process, where the first phase consists of ion arrival to the electrode and subsequent steps to form a solid deposit on it, and the second phase consists of the deposition process itself followed by partial dissolution of the deposit. The two phases correspond to the process of client-arrival and client-servicing in queuing theory. In particular, the M/M/1, the G/M/1 and the M/M/k queuing models are quantitatively compared in terms of queuing time and certain other queuing characteristics.

Keywords: *anodic dissolution*, *copper*, *oscillations*, *queuing theory*

List of symbols

$A(t)$	(arbitrary) probability density function in the G/M/1 model
$A^*(\mu, z)$	Laplace transform of $A(t)$ with transform variable $\mu(1-z)$
e_0	electric charge of a monovalent ion (0.1062 aC)
i	current density
L	mean number/expectation of participants in a queuing system
L_q	mean number/expectation of participants in a queue
N	random number of participants in a queuing system; n its numerical value
p	numerical value of a probability
Q	random number of ionic participants undergoing the electrode reaction
q	limiting value of a probability
$S(x)$	probability density function of random service time X in the M/G/1 model
s	mean value/expectation of random service time X in the M/G/1 model
T	random time; t its numerical value
X	random service time; x its numerical value
Y	random queuing time; y its numerical value

Greek letters

η	numerical value of the smallest root of Equation 24
Θ	random total time; θ its numerical value
λ	mean rate (or density) of process I
μ	mean rate (or density) of process II
ρ	traffic density, defined as λ/μ
τ	random transition time
ϕ	probability density function

Subscripts

i,j,k	process number or an integer value
I	denotes process I

Superscripts

o	initial value

Special symbols

CTU	characteristic time unit
E	mean value/expectation of a random variable
G/M/1	single server model with arbitrary probability distribution for process I, and negative exponential distribution for process II
IAR	ion arrival/reaction sequence
M/G/1	single server model with Poisson distribution for process I and an arbitrary probability distribution for process II
M/M/1	single server model with Poisson distribution for process I and negative exponential distribution for process II
M/M/k	k-server model with Poisson distribution for process I and negative exponential distribution for process II
P	probability
Var	variance of a random distribution
ε	a state of the random process
ξ	a random process

1. Introduction

Queuing theory is concerned with relating the magnitude of a queue to rates at which arrivals and servicing proceed. Ticket counters, automobiles at traffic lights, factory assembly lines, patients in a hospital emergency room etc. are the most obvious examples of queue formation. Although it is not immediately

0021-891X

obvious, queuing theory may serve for an interpretation of an electrode reaction [1] as a *servicing centre* for electrons arriving to the solid surface. In this view, the overpotential of an electrode reaction may be related to the electron queue at the solid–liquid interface. This particular interpretation is by no means the only application of queuing theory which might be envisaged for electrochemical phenomena. The purpose of this paper is to present an application of queuing theory to the oscillatory behaviour of a certain class of electrode reactions, where an electrode reaction/film formation sequence is followed by deposition and partial redissolution in a cyclic manner. Numerical illustrations are provided for a specific experimental anodic copper dissolution process.

One major incentive for the approach is to demonstrate the cross-fertilization of different disciplines. By adapting seemingly unrelated concepts of queuing theory to electrochemical phenomena, a set of conceptual 'equivalences' can be established for the sake of a quantitative analysis. This philosophy does not intend to dismiss traditional approaches, but it aims to support scant mechanistic information available in the case of complex process whose mechanism is poorly (if at all) understood.

2. Basic concepts and framework of analysis

Following the fundamental theory of queues [2–5], active centres on the electrode surface are considered to be a collection of servers; ions, particles and molecules participating in the electrode reaction → deposit formation → partial redissolution process are clients. In this framework, the overall physical process may be viewed as an arrival of clients to a collection of servers, followed by processing by the servers. Specifically, arrival into the queue may be interpreted as an ion arriving first at the surface, then undergoing an appropriate reaction or reaction sequence resulting in a compound (e.g., an oxide) ready for deposition on the active centres of the electrode surface. This part of the overall process is called 'phase I' in the sequel. Servicing represents the deposition/partial redissolution phase, resulting in the reappearance of an ion. This part of the overall process is called 'phase II' in the sequel. The arriving ions can move randomly towards any active centre, but it is assumed that *in the immediate vicinity* of the surface, each ion would move to the nearest centre. Thus, the electrode surface is regarded as a multiple set of (single) servers, each server acting simultaneously in the same manner. Hence, it is immaterial if a single deposition and dissolution step originates at the same site. In the simplest adaptation of the theory, it is sufficient to analyse the overall process in terms of a single-server queue with average rate λ for phase I and average rate μ for phase II, but multiple-server queues can also be envisaged, as shown in later Sections. The number of deposit particles formed during a finite time interval, and the length of time required for deposition/redissolution are taken to be random variables possessing specific individual probability distributions.

3. Analysis via the M/M/1 model for single-server queues

Consider first phase I. Within a certain time interval, the probability of more than one ion arriving and reacting is zero, and the probability of an ion arrival/reaction (IAR) is a finite number between zero and unity. If the occurrence of IAR is independent from one such time interval to another, then the probability distribution of IAR occurrences in a finite time interval x is Poissonian, for example,

$$P[N_\mathrm{I} = n] = (\lambda x)^n \exp(-\lambda x)/n! \quad n = 0, 1, 2, \ldots \tag{1}$$

with mean value $E[N_\mathrm{I}] = \lambda x$ and variance $\mathrm{Var}[N_\mathrm{I}] = \lambda x$. The time T elapsed between two adjacent IAR, equivalent to the concept of interarrival time in queuing theory, has an exponential distribution with probability density function $\lambda \exp(-\lambda t)$, that is,

$$P[T > t] = P[N_\mathrm{I} = 0 \text{ in } (0, t)] = \exp(-\lambda t) \tag{2}$$

where t is an arbitrary time instant. It follows that $E[t] = 1/\lambda$, and $\mathrm{Var}[T] = 1/\lambda^2$.

Consider now phase II. Let $i = 1$ be the index for the state of deposition pursuant to an IAR, and $i = 2$ the index for the state of redissolution, liberating temporarily an active centre. If $\xi(t)$ denotes the random deposition/redissolution process, then at zero time:

$$P[\xi(t) = \varepsilon_i] = p_i^\mathrm{o} \tag{3}$$

and

$$P[\xi(\delta + t) = \varepsilon_j \mid \xi(\delta) = \varepsilon_i] = p_{ij}(t) \tag{4}$$

indicating that phase II is a Markov process, provided that at an arbitrary time δ the state is either ε_1 or ε_2. It follows that

$$P[\tau > t] = \exp(-\mu t) \tag{5}$$

if τ is the random time required for the process to leave one state by going to the other state. It follows that $E[\tau] = 1/\mu$ and $\mathrm{Var}[\tau] = 1/\mu^2$.

The queue consists of $Q(t)$ number of ions undergoing reaction associated with the active centre; each active centre constitutes a reaction site for a single molecule. One molecule of the reaction product becomes a deposit upon service by the active centre, hence the number of participants in the process is $N(t) = Q(t) + 1$ (since one active centre can service only one molecule at any given time). Thus, if the rate of phase II exceeds the rate of phase I on an average, a steady state is finally established, and the limiting probability

$$p_n = \lim_{t \to \infty} [N(t) = n] = (1 - \rho)\rho^n; \quad \rho < 1 \tag{6}$$

shows a geometric distribution for N with parameter ρ. It then follows that under steady-state conditions, and for $\rho < 1$, the mean number of participants in the system is

$$L \equiv E[N] = \rho/(1-\rho) \tag{7}$$

and the mean number of participants in the queue is

$$L_q = L - \rho \tag{8}$$

Let Y be the random queuing time, that is, the time lapsed between the moment of arrival of an ion and the moment when deposition of the molecule originating with the ion commences. In an empty system $Y = 0$ with probability of occurrence

$$P[Y = 0] = 1 - \rho \tag{9}$$

With probability density function of queuing time

$$\phi(y) = \rho(\mu - \lambda)\exp[-(\mu - \lambda)y] \tag{10}$$

Equation 11:

$$P[Y = 0] + \int_0^\infty \phi(y)\mathrm{d}y = 1 \tag{11}$$

indicates that the random variable Y is partly discrete, partly continuous.

In a similar manner, the distribution of service time X and the total time $\Theta = Y + X$ may be analysed, with the following results. Since Θ has the probability density function

$$\phi(\theta) = (\mu - \lambda)\exp[-(\mu - \lambda)\theta] \tag{12}$$

the mean queuing time is given by

$$E[Y] = \lambda/[\mu(\mu - \lambda)] \tag{13}$$

and the mean total time is given by

$$E[\Theta] = E[Y] + E[X] = 1/(\mu - \lambda) \tag{14}$$

Hence, Equations 7 and 8 may be written alternatively as

$$L = \lambda E(\Theta) \tag{15}$$

and

$$L_q = \lambda E(Y) \tag{16}$$

4. Application of the M/M/1 model to the dynamics of anodic copper dissolution

The anodic dissolution of copper into certain aqueous electrolytes exhibits a quasi-periodic current oscillation over an intermediate time period [7]. Oscillation is due to a cyclic deposition/redissolution of copper oxides in the presence of small amounts of thiocyanate ions. The exact mechanism of this process is not understood at present, although basic chaos theory has tentatively been suggested as one possible avenue of interpretation [8]. Queuing theory offers a probabilistic means of analysing the cycling phenomenon, illustrated in Fig. 1 [9]. The oscillatory regime is flanked by a preoscillation and a postoscillation zone; in the former, steady-state service is not yet available, that is, the active centres on the surface are not yet fully activated. In the postoscillation zone the rates of phase I and phase II are essentially identical, resulting in a steady flow without queuing. The intermediate zone for oscillation is characterized by two different process rates. Phase I comprises (i) the 'arrival' (i.e., the appearance) of cuprous ions, due to anodic dissolution of copper metal at the surface and (ii) their oxidation to Cu_2O and CuO, and their reaction with thiocyanate ions to form CuSCN. The latter is quantitatively very small compared to oxide forming, since the thiocyanate ion concentration in the electrolyte is at the mmol/L level. Phase II comprises (i) the deposition of these copper compounds on the anode surface and (ii) the partial dissolution of the anode film liberating a portion of the anode for (continuing) anodic dissolution of copper metal. The peaks (i.e., the minimum and maximum values of the instantaneous current density) in Fig. 1 represent the highest and the lowest availability of active centres (i.e., servers).

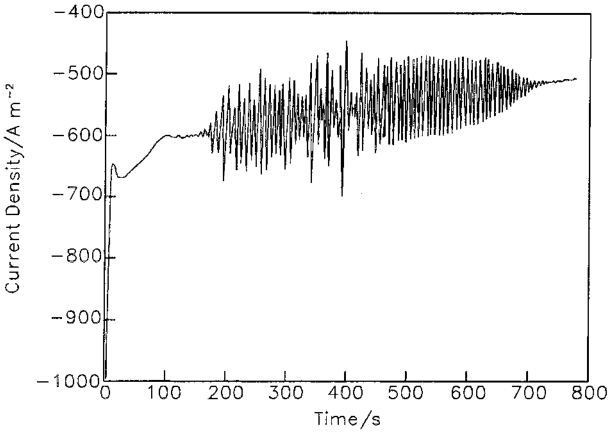

Fig. 1. A typical oscillation pattern observed during the anodic dissolution of copper into an aqueous 4 mol dm^{-3} NaCl/ 1 mmol dm^{-3} KSCN solution (pH 3.4) at an anodic overpotential of −60 mV vs SCE [9; Fig. 2].

The mean process rates were determined from the eighty one oscillatory cycles in Fig. 1, by measuring the slope of each half-cycle. Slopes pertaining to increasing current yield the mean rate of 8.68 mC cm^{-2} s^{-1} for ion-arrival to the electrode, and slopes pertaining to decreasing current yield the mean rate of 19.198 mC cm^{-2} s^{-1} for deposition/partial dissolution over the average half-cycle duration of 4 s. Assuming that the electrode reaction is a single electron transfer process (i.e., that cuprous ions are discharged in the electrode reaction to form cuprous oxide, which may partially be oxidized to CuO in a purely chemical step), the ionic flows are $\lambda = 8.68/e_0 = 5.418 \times 10^6$ ion s^{-1} (phase I) and $\mu = 19.98/e_0 = 12.47 \times 10^6$ ion s^{-1} (phase II) per cm^2 of the anode surface. The mean density ratio (i.e., traffic density in queuing theory) is $\rho = \lambda/\mu = 0.434$. It is convenient for a simplified computation to define a characteristic or reference time unit (CTU) which adjusts the process densities to values near unity, although this numerical value has no theoretical significance. Setting CTU = 10 as (i.e., 10^{-17} s), the process densities become $\lambda = 0.542$ ion/CTU and $\mu = 1.247$ ion/CTU

Table 1. The distribution of the number of participants N in a queue associated with an active centre in an anodic copper dissolution process [7]

N	*P*[*N* = *n*] (*Eq. 6*)*
0	0.566
1	0.246
2	0.107
3	0.0462
4	0.02
5	0.0087

* in steady state, assuming that the queue-formation transient is negligible

Table 2. The cumulative probability distribution of queuing time Y in an anodic copper dissolution process [7]

y (*CTU*)	$P[Y \leqslant y]$*
0	$P[Y = 0] = 0.566$ (Equation 9)
1	0.785
2	0.894
3	0.948
4	0.974
5	0.987

* $P[Y \leqslant y] = P[Y = 0] + 0.434[1 - \exp(-0.705y)]$

per cm^2 of the anode surface (with $\rho = 0.434$ unchanged). The queue characteristics obtained via the M/M/1 model are: $p_n = 0.434^{n+1.467}$ (Equation 6); $L = 0.767$ (Equation 7); $L_q = 0.333$; $E(Y) = 0.616$ CTU or 6.16 as (Equation 13) and $E(\Theta) = 1.418$ CTU or 14.18 as (Equation 14). Tables 1 and 2 provide pertinent probability distributions.

5. Analysis

5.1. *Effect of active centre/server population on queue characteristics*

It was pointed out earlier that the single-server approach is based on the postulate of the electrode surface containing a multiple set of identically functioning single active centres/servers. If this postulate is relaxed, each participant in phase I can have a choice of several adjacent servers and the M/M/k queuing model may be invoked, where k is the number of servers. Although k is *a priori* unknown, it is possible to estimate the probability that an exactly j number of servers is occupied at any given time by the Erlang formula [3]:

$$p_j = (1/j!)\rho^j \Big/ \sum_{j=0}^{k} (1/j!)\rho^j \quad j = 0, 1, 2, \ldots \tag{17}$$

which yields for the anodic dissolution of copper the probabilities $p_0 = 0.566$; $p_1 = 0.246$; $p_2 = 0.107$; $p_3 = 0.046$ and $p_4 = 9.58 \times 10^{-4}$. Thus, there is an about 19% probability that more than one server, an about 8% probability that more than two servers, and an about 3.5% probability that more than three servers are engaged at any given time. As shown in Table 3, the M/M/k model predicts an increasingly more efficient service by the active centres; in the limit, the mean total time tends to the reciprocal of the service density, $1/\mu$, indicating that if the number of active centres is very large, the time spent in the queue during phase I tends to zero and the rate of the overall process is determined essentially by the rate of phase II. The two-server model is, in fact, quite adequate for the estimation of L and $E(\Theta)$, since the total number of active centres available for service has a very small effect on either characteristic for $k \geqslant 2$.

5.2. *Application of the M/G/1 model*

The M/G/1 model retains the Poisson distribution for phase I with mean rate λ, but it allows the service time X to have an (*a priori*) arbitrary probability density function $S(x)$ with mean value

$$s = \int_0^\infty x S(x) \mathrm{d}x \tag{18}$$

Table 3. The effect of server population on the queuing system characteristics in an anodic copper dissolution process [7]; *M/M/k models*

Characteristic	*Service* (*active centre*) *availability per participant, k*			
	1	*2*	*3*	*4*
Probability of not more than k servers being engaged at a given time	0.812	0.919	0.965	0.966
Mean number of participants in the queue, L_q	0.333	0.0215	0.00175	0.00013
Mean number of participants in the system, L	0.767	0.455	0.436	0.434
Mean value of queuing time, $E(Y)$/as	6.16	0.396	0.0323	0.00239
Mean value of total time, $E(\Theta)$/as	14.18	8.39	8.04	8.02

$\lim E(Y) = 0$; $\lim E(\theta) = 1/\mu$; $\lim L = \rho$ as $k \to \infty$

If the random number N_n denotes the number of participants joining the queue during the time spent by the nth participant in the system, the probability that N_n has a specific value k is given by Equation 19:

$$P[N_n = k] = (1/k!)\int_0^{\infty} (\lambda\theta)^k \exp(-\lambda\theta)\phi(\theta)\mathrm{d}\theta \qquad (19)$$

where $\phi(\theta)$ is the probability density function for the time spent by the nth participant in the system. The establishment of $S(x)$ and $\phi(\theta)$ for phase II can be effected in principle by classical means of identification from experimental data [e.g., 11, 12], but the procedure is time consuming.

5.3. *Application of the G/M/1 model*

In the G/M/1 model, the random interarrival time for participants in phase I has an arbitrary probability density function $A(t)$, and service time in phase II has a negative exponential distribution with mean rate μ. If Q_n is the number of participants already in the system as nth participant arrives, then the probability that Q_n is exactly a number k (at steady state) is $q_k \equiv \lim P[Q_n = k]$ for large n, and the probability that an exactly j number of participants is engaged in phase II during any interarrival interval is

$$p_j = (1/j!)\int_0^{\infty} (\mu t)^j \exp(-\mu t)A(t)\mathrm{d}t \qquad (20)$$

The two probabilities are related by the expression

$$q_k = \sum_{i=0}^{\infty} q_{i+k-1} p_i \quad k = 1, 2, 3, \ldots \qquad (21)$$

with

$$q_0 = \sum_{i=0}^{\infty} q_i \xi_i \qquad (22)$$

where ξ_i is the probability that more than j participants undergo phase II in an interarrival interval. It may be shown upon an involved derivation [13] that

$$q_k = (1-\eta)\eta^k \quad k = 0, 1, 2\ldots \qquad (23)$$

where η is the smallest root of the algebraic equation

$$z = A^*(\mu; z) \qquad (24)$$

and A^* is the Laplace transform of $A(t)$ with transform variable $\mu(1-z)$. The queue characteristics may be calculated as $L = \eta/(1-\eta); E(Y) = \eta/[\mu(1-\eta)]$ and $E(\theta) = 1/[\mu(1-\eta)]$.

6. Discussion

It follows from the preceding paragraphs that the knowledge of the probability distribution of random variables in phase I and phase II is required for the use of queuing theory. The first question to ask is whether service-time associated with phase II can be assumed to possess a negative exponential distribution, that is, if Equation 5 is appropriate. To prove that it is [14], let $\Psi(x)$ be a function of time, representing the probability that service time X is larger than a chosen time t. If X is larger than an arbitrary time instant t_1, then the conditional probability is given by

$$P[X > (t + t_1) \mid X > t_1] = \Psi(t) \qquad (27)$$

since the process will be in the same state at time $(t + t_1)$ as at time t_1. It follows from the basic theorem of conditional probabilities (e.g., [15]) that

$$P[X > (t + t_1)] = P[X > (t + t_1) \mid X > t_1]P[X > t_1]$$

or, alternatively, that

$$\Psi(t + t_1) = \Psi(t)\Psi(t_1) \qquad (28)$$

that is,

$$\log \Psi(t + t_1) = \log \Psi(t) + \log \Psi(t_1) \qquad (29)$$

for arbitrary t and t_1. As shown by Feller [16], Equation 29 implies that $\log \Psi(t) = -kt$, apart from the trivial result of $\log \Psi(t) = 1$. Equation 5 immediately follows from this result.

A second concern is the probability distribution appropriate for phase I. The assumption made in Section 3 about the Poisson distribution of the number of participants engaging in the queuing process may be supported by the argument that this process resembles nucleation, where the Poisson distribution has previously been proposed for site activation [17] and the formation of a new phase [18]. Since the time-lapse distribution is a single-parameter negative exponential function (see Equation 2) in this case, one could argue that a two-parameter gamma-distribution might offer a more realistic interpretation of phase I with probability density function

$$\phi(t) = [1/\Gamma(\alpha)\beta^{\alpha}]t^{\alpha-1} \exp(-t/\beta) \qquad (30)$$

carrying $E(T) = \alpha\beta$ and $\mathrm{Var}(T) = \alpha\beta^2$. From the experimentally determined values of the reciprocal of the mean rate, 1.845 CTU and its standard deviation of 3.035 CTU, the parameter estimates $\alpha \approx 0.4$ CTU and $\beta \approx 5.0$ CTU are computed. Then, taking the G/M/1 model and following the procedure shown in Section 5.3, the queue characteristics $\eta = 0.611$; $L = 1.571$; $E(Y) = 1.259$ CTU (12.59 as) and $E(\Theta) = 2.061$ CTU (20.61 as) are obtained. Comparison with the M/M/k queue models (Table 3) indicates that the M/M/2 and M/M/3 models somewhat overestimate the efficiency of the overall process; reasonable agreement between the M/M/1 and the G/M/1 (G: gamma distribution) model suggests that the single-server model offers an admissible *probabilistic* description of the anodic copper dissolution process. The consistently larger numerical values of queue parameters in the G/M/1 model suggest nevertheless that the variance of the rate estimates might be too large for the employment of a single-parameter model based only on the mean value of the experimental rate of oscillation.

In summary, the M/M/1 model yields the following interpretation of the overall process, under the experimental conditions indicated in Fig. 1: on an average, the $Cu^+ \rightarrow Cu_2O/CuO$ sequence requires about 6 as (attoseconds) per cuprous ion, and about 14 as for one oxidation → deposition → partial redissolution cycle. There exists, on an average, a small queue prior to oxide deposition (since the predicted number of ions/oxides waiting in the queue is 0.33). The mean number of Cu_2O or CuO molecules in the *overall* process is about 1.5. The G/M/1 (G: gamma distribution) model predicts about 1.3 as for the $Cu^+ \rightarrow Cu_2O/CuO$ sequence and about 2 as for the overall process. The $M/M/k$ models predict an essentially empty queue and an asymptotic tendency towards the limiting mean number of participants in the system ($\rho = 0.434$) and the limiting mean value of the total time ($1/\mu = 8.02$ as), as k is increased. Both limiting values are practically reached at $k = 3$. It is instructive to note that in classical theory the time required for electron transfer at an electrode is e_0/i, that is, about 160 as at $i = 1\,\mathrm{mA\,cm^{-2}}$ for a monovalent ion participating in a *nonoscillatory* electrode reaction.

7. Final remarks

The material presented here demonstrates only an elementary application of queuing theory to complex electrode processes. The exploration of advanced aspects of the theory (e.g., [19–21]), although an inviting challenge to electrochemical researchers interested in probability theory, is beyond the scope of this paper. Probability-based approaches do not obviate the need for deterministic experimental research (costly as it may be), but they provide an alternative interpretation of experimental observations related to processes whose exact mechanism is unknown.

Acknowledgement

Author's research in this area has been supported by the Natural Sciences and Engineering Research Council of Canada (NSERC).

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