Journal of Applied Electrochemistry **29**: 1125–1128, 1999.

Short Communication

An application of the Pollaczek–Khintchine theorem of queuing theory to the dynamics of anodic dissolution

T.Z. FAHIDY
Department of Chemical Engine397bering, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

Received 8 December 1997; accepted in revised form 9 February 1999

Key words: deposition, dissolution, ion arrival, queuing theory

List of symbols

a	Geary statistic
$\sqrt{b_1}$, b_2	Fischer–Pearson statistics
$E[X]$	expectation of random variable X
$E[q]$	mean number of participants in the system
$E[W]$	mean value of queuing time
E_o	fundamental electric charge (1.602×10^{-19} C)
I	current density
L_q	expected number of participants in a queue, $\lambda E[W]$
n_i^*	number of ions arriving over a 100 as time period at the mid-point rate in the ith interval
n_i	the value of n_i^* rounded to the nearest integer
N_i	the observed number of occurrences in the ith interval
N_i'	the number of occurrences in the ith interval estimated via a Poissonian distribution
P_i	Poissonian probability of arrival in the ith period
R	ratio of the average waiting time to service time (Equation 3)
q	number of participants left in a queue by a departing participant, including the participant being served
S	sensitivity factor (Equation 4)
T	time required for dissolution producing a cuprous ion
W	queuing time
z_I	ionic valency

Greek symbols

λ	mean rate of arrival
μ	mean rate of service
χ^2	symbol for a chi-square statistic in probability theory
ρ	traffic density, λ/μ

1. Introduction

As demonstrated in a recent application of queuing theory to anodic dissolution dynamics [1], the anodic dissolution of copper into aqueous NaCl solutions containing small amounts of thiocyanate ions may be modelled (as an alternative to nonprobabilistic approaches) as a queuing process. In this view, the previously presented model postulates a Poissonian distribution of ion arrival/electrode reaction (phase I), and an exponential distribution of surface-deposit dissolution time (phase II), as an equivalent of client-arrival and client-servicing in queuing theory. The purpose of this account is to analyse the effect of relaxing the requirement of exponential service-time distribution in Phase II on certain queue characteristics, and to provide a numerical illustration in the case of the copper dissolution process.

Figure 1 [1], reproduced here as Figure 1, illustrates a typical oscillation pattern observed in an experimental laboratory-scale cell. The preoscillatory zone represents an induction (or 'incubation') period where the active centres of the anode surface are becoming activated. The oscillatory zone represents two alternating phases. In phase I cuprous ions appear at the surface and are oxidized to essentially Cu_2O, with some partial oxidation to CuO, and the formation of CuSCN; the small amount of SCN^- ions is important for the induction of oscillation. In phase II the copper compounds form a deposit layer on the anode surface; partial dissolution of this anodic layer liberates a portion of the surface for continuing dissolution of metallic copper. In the post-oscillatory period the two process rates are essentially equal, hence a queue is not formed. In the companion paper [1] the interpretation of the anodic dissolution process in terms of a single server model (M/M/1) was discussed in specific detail. The model postulates a Poisson distribution for phase I, and a negative exponential distribution for phase II, with mean flow rates of λ and μ, respectively. The mean rates were determined from the eighty one cycles making up the oscillatory zone in Figure 1, using measured slopes of each half cycle, and the fact that the ionic flux is the reciprocal of the $z_I e_o$ product (with a numerical value of $6.24 \times 10^{15}\, I$ ion $s^{-1}\,cm^{-2}$ when $z_I = 1$ and I is expressed in mA cm^{-2} units). The mean flow rates, computed as $\lambda = 5.418 \times 10^{16}$ and $\mu = 12.47 \times 10^{16}$ ion $s^{-1}\,cm^{-2}$

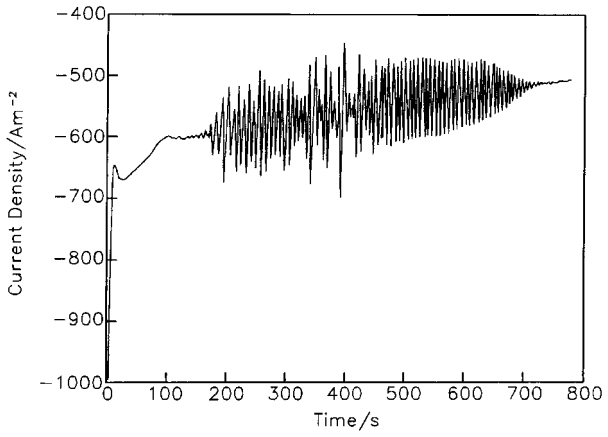

Fig. 1. Experimentally observed current density against time variation during the anodic dissolution of copper (Figure 1 in [1]).

yield the mean density ratio (i.e., traffic density in queuing theory) of $\rho = \lambda/\mu = 0.434$. These numbers form the basis for a queuing theory-based analysis of the dissolution process.

2. Summary of the Pollaczek–Khintchine (PK) theorem and its application to the anodic dissolution of copper

The PK theorem [2] indicates for a queuing process with random arrivals possessing a Poisson distribution that, if the (theoretical) probability distribution of the service time is unknown, it is sufficient to consider the mean and the variance of the *empirical* service-time distribution for the estimation of the expectations:

$$E[q] = \rho + \left(\rho^2 + \lambda^2 \operatorname{Var}[T]\right)/2(1-\rho) \tag{1}$$

and

$$E[W] = \left(\rho^2 + \lambda^2 \operatorname{Var}[T]\right)/2\lambda(1-\rho) \tag{2}$$

This important theorem implies that only the first two statistical moments, and not the entire moment spectrum of the service-time distribution need to be known [3]. A short and elegant proof of the PK theorem is given by Franken et al. [4]. If the service time does happen to have an exponential distribution, then $\operatorname{Var}[T] = 1/\mu^2$ and the queue characteristics of the M/M/1 process are obtained. In applying the PK theorem to the copper dissolution process, it is first shown that phase I is, indeed, poissonian. It is convenient to work with an attosecond time scale $\left[1\,\text{as} \equiv 10^{-18}\,\text{s}\right]$ at this stage, which yields the numerical values of $\lambda = 0.0542$ ion $(\text{as})^{-1}\,\text{cm}^{-2}$ and $\mu = 0.1247$ ion $(\text{as})^{-1}\,\text{cm}^{-2}$. In order to deal with a convenient range of 0–20 arrival incidences, a base interval of 100 as is chosen. As shown in Table 1, ten base intervals with different ionic arrival rates, and the number of intervals having the same arrival rates are established. The computed values are compared to the number of ionic arrivals estimated via a poissonian model with mean of 5.42. The experimental value of $\chi^2 = 15.86$ being essentially identical to the critical value at the 97.5% level of confidence $\left[\chi^2(7;\,0.025) = 16.0\right]$, phase I may be considered to be poissonian, accordingly, the PK theorem may be applied (put more carefully, the null hypothesis that the distribution is poissonian cannot be rejected at a highly significant (99%) level of confidence).

Table 1. Test for the hypothesis of poissonian ion arrival in the oscillatory zone of Figure 1

n_i^*	n_i	N_i	P_i	N_i'	Y_i^2
0.625	1	5	0.0240	1.944	4.804
1.87	2	4	0.0650	5.267	0.304
3.13	3	9	0.1175	9.516	0.080
4.37	4	19	0.1591	12.894	2.891
5.63	6	18	0.1559	12.626	2.296
6.87	7	16	0.1207	9.776	3.962
8.12	8	5	0.0818	6.623	0.398
9.37	9	3			
13.10	13	1	0.0495	4.004	0.247
18.10	18	1			

Legend: $Y_i^2 = \left(N_i - N_i'\right)^2/N_i$; $\chi^2 = \Sigma_i Y_i^2 = 14.98$
$P_i = (5.42)^n \exp(-5.42)/(n_i!)$

In analysing the service-time distribution, the mean rate of $\mu = 0.1247$ ion $(\text{as})^{-1}\,\text{cm}^{-2}$ is computed from the dissolution half-cycles shown in Figure 1. In the companion paper [1] this value was employed as the rate parameter in phase II for which the exponential distribution was taken as a first approximation. The postulate stems from the assumption that the electrode surface behaves as a markovian process generator [5]. The importance of the PK theorem becomes evident at this point; the postulate of exponential distribution becomes immaterial, and the queue characteristics are computed on the basis of the experimental variance of dissolution times assembled in Table 2. The parameter estimates resulting from this computation are shown in Table 3.

Table 2. Experimental service time distribution of the anodic copper dissolution process*

1–20	21–40	41–60	61–80
8.26	7.42	8.66	7.42
4.13	8.67	8.26	11.55
8.26	7.42	8.26	10.30
10.30	9.48	8.26	8.66
4.13	6.19	10.30	7.42
7.42	8.26	8.26	8.26
6.19	9.08	7.42	8.26
8.26	10.72	8.26	7.02
7.42	10.72	8.26	10.72
7.84	7.02	11.15	8.26
10.30	7.42	7.42	7.84
7.42	6.19	7.42	7.42
8.26	4.95	8.26	8.66
8.26	4.95	8.26	7.84
10.30	6.19	8.26	7.02
7.84	8.26	8.26	6.19
9.08	7.42	10.30	6.19
8.66	8.26	8.26	6.59
7.42	8.66	8.26	6.19
8.26	5.77	10.30	

* Values are given in attosecond (as)

Table 3. Queue characteristics predicted by the M/M/1 model and the PK theorem for the anodic copper dissolution process

Characteristic and its unit	M/M/1 model	PK theorem (mean based)	PK theorem (median based)
Mean service time (as)	8.02	8.02	8.02 Median = 9.38
Variance of service time $(as)^2$	64.31*	2.235	2.235
$E[q]$	0.767	0.606	0.684
L_q	0.333	0.172	0.227
$E[W]$ (as)	6.16	3.18	3.95
R	0.767	0.397	0.456

* $\mathrm{Var}[T] = 1/\mu^2$

3. Discussion

The electrochemical interpretation of the queuing theory-based results is straightforward. Under the experimental conditions related to Figure 1, the mean rate of arrival of cuprous ions and subsequent deposition of their oxide formed at one cm^2 of anode surface area is $\lambda = 0.0542$ per attosecond (phase I). Redissolution of the oxide and the reappearance of cuprous ions proceeds at a mean rate of $\mu = 0.1247$ per attosecond (phase II). The mean number of ions in the system comprising the two phases is $E[q]$, the mean number of ions in the queue is L_q, and their mean queuing time is $E[W]$. These quantities may be considered as kinetic parameters of the formation/dissolution cycle.

The queue parameters assembled in Table 3 indicate that the M/M/1 model overestimates the expected value of queuing time, and slightly overestimates the number of participants in the queue and in the system, with respect to the Pollaczek–Khintchine predictions. It is instructive to include parameter estimation based on median service time in lieu of the mean service time (fourth column in Table 3). The median is another measure of the centre of distribution in as much as the probability of a service time being below or above the median is exactly one-half. One advantage of the median over the mean is that the median is less sensitive to extreme values (or outliers) than the mean [6]. The median based values in Table 3 are numerically closer to the M/M/1 model values, but not particularly different from the mean based values. The last row contains estimates of the ratio of the average waiting time to service time, computed as [2]

$$R = \rho\big(1 + \mu^2\,\mathrm{Var}[T]\big)/2(1-\rho) \tag{3}$$

The knowledge of R permits an estimation of the sensitivity of the average waiting time to the numerical value of the traffic density related to the dissolution process. A further parameter, the sensitivity factor may be expressed as [2]

$$S = 1 + E\big[d^2\big]/\rho_m(1-\rho_m)^2 \tag{4}$$

where $d \equiv \rho - \rho_m$; ρ_m is the mean value of traffic density computed from an ensemble of experimentally determined values of ρ. If, for instance, three experimental oscillograms (similar to Figure 1) were available with computed ρ values of 0.415, 0.428 and 0.459, hence $\rho_m = 0.434$ and $E\big[d^2\big] \approx 0.001$, this would indicate an about 0.7% increase in the average waiting time in the queue. Although immaterial for the employment of the PK theorem, it is instructive to note that the experimental dissolution times fit quite closely a normal distribution with Fisher–Pearson statistics of $\sqrt{b_1} = 3.583$; $b_2 = 16.32$, and Geary statistic of $a = 0.547$ [7], but with considerable skewness and a leptokurtic tendency.

4. Final remarks

The application of the PK theorem enhances the usefulness of queuing-theory principles in the interpretation of certain electrode processes, where particles are considered as clients (or consumers) and the active centres on the electrode surface as client servers. In the anodic dissolution considered here, an alternative analysis in terms of an M/G/1 model (where code G denotes service time with normal distribution) is possible in principle, but is unnecessary. Moment-generating functions of experimental service time distributions are not needed, hence queue characteristics can be estimated at relative ease without lengthy computations. Further opportunities of employing queuing theory to electrochemical phenomena (such as birth–death, immigration–emigration, immigration–death (e.g., [8]) applied to electron transfer, surface deposit transformations and residence time distribution in electrolysers) remain to be explored in the effort of bringing different disciplines together.

Acknowledgement

This research has been supported by the Natural Sciences and Engineering Research Council of Canada (NSERC).

References

1. T.Z. Fahidy, 'An application of queuing theory to the dynamics of anodic dissolution', *J. Appl. Electrochem.* **28** (1998) 411.
2. T.L. Saaty, 'Elements of Queuing Theory With Applications' (Dover, New York, 1961); Section 2–5b, pp. 40–43.

3. W.C. Griffin, 'Queuing: Basic Theory and Applications' (Grid Inc., Columbus, Ohio, 1978), Chapter 9, pp. 173–198.
4. P. Franken, D. Koenig, U. Arndt and V. Schmidt, 'Queues and Point Processes' (J. Wiley & Sons, New York, 1982), Section 4.5.5, pp. 129–130.
5. Y.A. Rozanov, 'Probability Theory: A Concise Course' (Dover, New York, 1977), Chapter 8, pp. 102–114.
6. S.F. Arnold, 'Mathematical Statistics' (Prentice Hall, Englewood Cliffs, NJ, 1990), Section 3.5, pp. 131–132.
7. E.S. Pearson and H.O. Hartley (Eds), 'Biometrika Tables for Statisticians' Vol.I (Cambridge University Press, London, 1958), Section 17, pp. 61–63; Table 34, p. 183; Table 35, p. 184.
8. D.R. Cox and H.D. Miller, 'The Theory of Stochastic Processes' (Chapman & Hall, London, 1970), Chapter 4, pp. 146–202.