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The application of renewal theory to anodic dissolution processes

T. Z. FAHIDY

Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

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The oscillatory behaviour of a certain class of dissolution processes involving anodic dissolution of a metal and the formation of a passivating substance is analysed in terms of renewals via isomorphism with a Type I counter in queuing theory.

Nomenclature

$E(X)$	statistical expectation of random variable X
E_i	expected frequency in the ith class of observation (due to a postulated probability distribution)
m	renewal number
N_t	number of renewals in time period (0, t)
O_i	observed frequency in the ith class observation
$R(t)$	renewal function (Equation 3)
T_m	time lapsed until the mth renewal
t	time
ρ	density parameter of the experimental probability density function
$\phi(u)$	Gaussian probability density function of random variable u
χ^2	chi-square statistic

1. Introduction

Anodic dissolution processes have recently drawn a good deal of attention as a particularly attractive area of application for modern stability theory, especially one of its newest branches, chaos dynamics [for example, 1-4]. The dissolution of copper in phosphoric acid [5] served as one appropriate case where the deterministic component of its overall behaviour is studied in terms of appropriate Poincaré sections of its phase portraits. Although a direct understanding of a physical mechanism derived *solely* from stability studies has not yet been generally demonstrated, such approaches hold promise for the analysis of surface and hydrodynamic phenomena influencing the overall dissolution process.

An alternative approach to the analysis of anodic dissolution may be sought via renewal theory, a domain of the mathematics of probabilities. Developed orginally to study failure and component-replacement problems, renewal theory has found application in various unrelated areas possessing similar probabilistic structures [6]. The purpose of this paper is to portray the scope of renewal theory in analysing a certain class of anodic dissolution, whose overall behaviour is traced through characteristic parameters of an equivalent process.

2. Basic theory

The fundamental tenet of the approach is summarized in Table 1: the dissolution process and a Type I counter [7] exhibit structural isomorphism if a substance dissolves anodically, then a second substance (passivator) blocks a dissolution site temporarily, liberating some time later the site upon its desorption for dissolution. The dissolution process is considered to be a sequential repetition of this cycle with the time of blockage possessing a certain probability density function (PDF). For a Type I counter the occurrence of arrivals is a Poisson process occurring at rate ρ and the PDF of arrival times is $\rho \exp(-\rho t)$, an exponential distribution. This renewal scheme can, therefore, be analysed in terms of probability theory, where the following parameters are of specific importance:

(i) N_t – the number of renewals in time period (0, t), which possesses a Poisson distribution with $\mu = \rho t$ and $\sigma = (\rho t)^{1/2}$. The probability of exactly m renewals occurring in (0, t) is

$$\Pr[N_t = m] = \frac{(\rho t)^m \exp(-\rho t)}{m!}; \quad m = 0, 1, 2, \ldots \tag{1}$$

and the relationship

$$\Pr[N_t < m] = \sum_{j=0}^{m-1} \frac{(\rho t)^j \exp(-\rho t)}{j!} \tag{2}$$

yields the probability of less than m renewals in the (0, t) time period. The expectation of N_t is, in this case, simply the (ρt) product, known as the *renewal function*; $R(t)$.

$$R(t) \equiv E(N_t) = \sum_{m=0}^{\infty} m \frac{(\rho t)^m \exp(-\rho t)}{m!} = \rho t \tag{3}$$

If t is sufficiently large, Equation 2 may be approxi-

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Table 1. The structural isomorphism of an anodic dissolution process and a Type I counter [7]

Dissolution process	*Type I counter*
A. At zero time the second substance (passivator) occupies site until time t_1; there is no dissolution of the first substance in $[0, t_1)$.	A. At zero time the counter is blocked until time t_1; no arrival is recorded in t_1.
B. At $t = t_1$ the passivator detaches from the site and dissolution proceeds in time t_1', independent of t_1.	B. At $t = t_1$ the counter is open and an arrival in time is t_1' registered, independent of t_1.
C. The site is blocked again by the passivator until time t_2, independent of t_1.	C. The counter is blocked until time t_2, independent of t_1.
D. At $t = t_2$ the site is free again due to detachment and dissolution proceeds in time t_2', independent of t_2.	D. At $t = t_2$ and counter is open again and an arrival in time t_2', independent of t_2, is registered.

mated by the expression

$$\Pr[N_t < m] \simeq 1 - \phi\left(\frac{t - m/\rho}{m/\rho}\right) \tag{4}$$

where $\phi(u)$ is the Gaussian normalised cumulative distribution function:

$$\phi(u) \equiv \frac{1}{(2\Pi)^{1/2}} \int_{-\infty}^{u} \exp - \left(\frac{x^2}{2}\right) \mathrm{d}x \tag{5}$$

(ii) T_m — the time lapsed until the mth renewal. By the equivalence of probabilities

$$\Pr[N_m > r] = \Pr(T_m < t_m)$$

the probability that for a specified M number of renewals the time is less than a specified time t_m is given by

$$\Pr[T_m < t_m] = \sum_{j=r}^{\infty} \frac{(\rho t_m)^j \exp(-\rho t_m)}{j!} \tag{6}$$

in the case of a Poisson type renewal process. If t is sufficiently large, Equation 6 may be approximated by the normal distribution:

$$\Pr[T_m < t_m] = \phi \frac{(t_m - m/\rho)}{(m^{1/2}/\rho)} \tag{7}$$

This approximation is especially useful if (ρt_m) is not an integer, since cumbersome interpolation of Poisson distribution tabulations would otherwise be necessary.

3. Application

If an anodic dissolution process may be modelled as a Type I counter, the PDF of the time lapsed from surface blockage, that is, the occupation of a site by the passivator until the full evolution of the dissolution of the first substance, has to be exponential. The test for the exponential nature of the PDF has two steps. First, the histogram of the frequency of time registered for the current to read a maximum value from its previous minimum value (see Fig. 1) is established. The second step consists of the examination of the hypothesis by a 'goodness-of-fit' test that the experimentally obtained histogram can be approximated at a certain confidence level by an exponential distribution. Employing the conventional chi-square test [8], if the test statistic

$$\chi^2 = \sum_{i=1}^{J} \frac{(O_i - E_i)^2}{E_i}$$

$$J = \text{number of histogram cells} \tag{8}$$

is less than the critical values at confidence level α and degree of freedom $v = J - 2$ of the tabulated chi-square distribution, the hypothesis cannot be rejected (at the level α). Then, the analysis described in the previous section can be applied directly.

4. Numerical illustration

Figure 1 depicts the variation of current with time in an hypothetical anodic metal dissolution process where the anodically produced cation forms a precipitate with one of the electrolyte anions. The precipitate temporarily occupies a certain portion of the anodic surface, causing a drop in the current, but it is detached from the surface at random time intervals due to convective motion of the electrolyte. Metal continues to dissolve at the liberated sites and the current increases until the next onset of precipitate deposition. The cycle is repeated over a certain time period (for example, the duration of a laboratory experiment).

Table 2. Statistical evaluation of the current oscillation in Fig. 1. 'Goodness-of-fit' test for the exponential distribution: PDF = $\rho \exp(-\rho t)$; $\rho = 4.545\ \mathrm{min}^{-1}$

Cell number	*Time interval, min.*	*Number of observed occurrences, O_i*		$p_i(t)$	E_i	
1	0–0.1	9		0.3652	10.957	
2	0.1–0.2	7	12	0.2319	6.956	11.373
3	0.2–0.3	5		0.1472	4.417	
4	0.3–0.4	4	9	0.0936	2.809	5.704
5	0.4–0.5	3		0.0589	1.768	
6	0.5–0.6	2		0.0376	1.127	

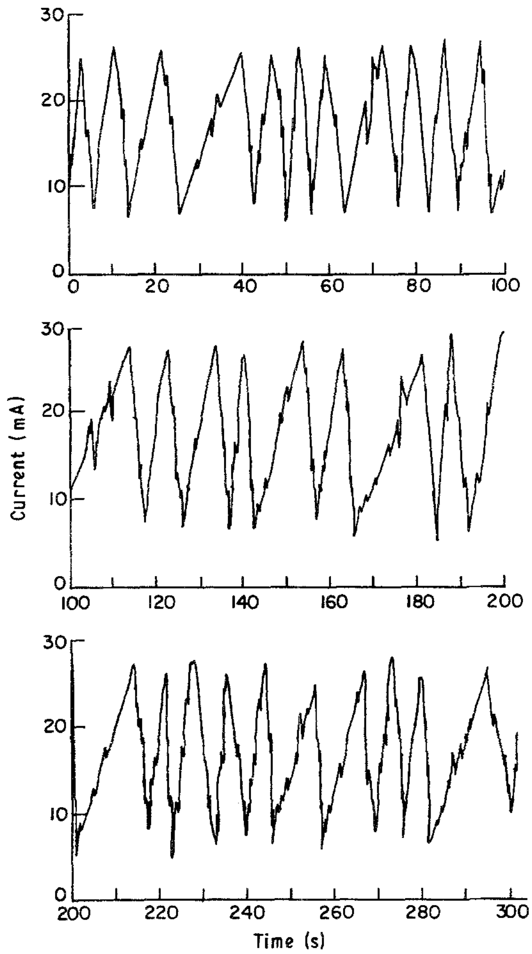

Fig. 1. An empirical current oscillation graph for the numerical illustration.

The analysis of the experimental frequency distribution of the times for the current to reach its maximum value from its previous minimum value is summarized in Table 2. The expected number of times in each cell was computed by multiplying the total number of observations with the integral of the postulated expotential PDF with density $\rho = 4.545$ min^{-1}, computed from the observed data:

$$E_i = 30\,[\exp(-4.545\,t_{i-1}) - \exp(-4.545\,t_i) \tag{9}$$

Combining the second and third, and the fourth, fifth and sixth cells in order to maintain a sufficiently high frequency in each cell [9], the chi-square statistic is computed as

$$x^2 = \frac{(10.957 - 9)^2}{10.957} + \frac{(11.373 - 12)^2}{11.373} + \frac{(5.704 - 9)^2}{5.704} = 2.289$$

in accordance with Equation 8. The degree of freedom being $3 - 2 = 1$, the critical values of the chi-square distribution 3.841 ($\alpha = 0.05$); 2.706 ($\alpha = 0.10$) and 1.323 ($\alpha = 0.25$) indicate that the hypothesis of the exponential substitution (with $\rho = 4.545\,\text{min}^{-1}$) fitting the experimental observations can be rejected only at a non-significant level of confidence (the computed $\chi^2 = 2.289$ is critical at $0.12 < \alpha < 0.13$) [10].

$$p_i(t) = \exp(-4.545\,t_{i-1}) - \exp(-4.545\,t_i)$$

$$\rho = 30/[9(0.05) + 7(0.15) + 5(0.25) + 4(0.35) + 3(0.45) + 2(0.55)] = 4.545\,\text{min}^{-1}$$

Consequently, the dissolution process can be assigned a Type I counter-equivalent with a renewal density (density of site liberation or the dissolution of the first substance) of 4.545 min^{-1}, or mean renewal time of 0.22 min. Further characteristics are assembled in Tables 3–5; the latter demonstrates the gradually diminishing discrepancy between the normal approximation and the rigorous Poisson model, as t_m increases.

Table 3. The probability of the occurrence of exactly m *number of dissolution renewals during time periods* (0, t)

m	$Pr\ (N_{t=m})$ (*Eqn* 1) $t^* = 1/\rho$	$t^\dagger = 2/\rho$
0	0.368	0.135
1	0.368	0.271
2	0.184	0.271
3	0.061	0.180
4	0.015	0.090
5	0.003	0.040

* Time equals the mean renewal time. $E(N_t) = 1$.
† Time equals the mean renewal time plus its standard deviation. $E(N_t) = 2$.

5. Discussion

The usefulness of the renewal theory-based approach is particularly manifest by the rapidity of detection of changes in dissolution mechanism, for example, the influence of an external field. Such changes would be identified via a strong numerical shift in the density of the exponential PDF of the dissolution, with respect to the reference case. Failure of a 'goodness-of-fit' test to indicate that an exponential distribution can fit the experimental current-frequency histogram at an acceptable level of statistical accuracy would demonstrate a serious structural change in the dissolution mechanism. Under certain circumstances, however,

Table 4. The probability of the number of dissolution renewals being less than m *during time periods* (0, t)

m	$Pr\ (N_{t<m})$ (*Eqn* 2) $t^* = 1/\rho$	$t^\dagger = 2/\rho$
1	0.736	0.406
2	0.920	0.677
3	0.981	0.857
4	0.996	0.947
5	0.999	0.983

*† See footnotes in Table 3.

Table 5. The probability of the time of the m th renewal time being less than t_m as a function of m

m	$Pr\ (T_m < t_m)$*						
	$t = 1/\rho$		$t = 2/\rho$		$t = 3/\rho$		$t = 1$
	Eqn 6	*Eqn 7*	*Eqn 6*	*Eqn 7*	*Eqn 6*	*Eqn 7*	*Eqn 7*
1	0.632	0.500	0.865	0.841	0.950	0.977	0.999
2	0.264	0.239	0.594	0.500	0.801	0.761	0.964
3	0.080	0.125	0.323	0.281	0.577	0.500	0.813
4	0.019	0.067	0.143	0.159	0.353	0.308	0.606
5	0.004	0.037	0.053	0.090	0.185	0.189	0.421
6	0.001	0.021	0.017	0.052	0.084	0.111	0.274
7	10^{-4}	0.005	0.005	0.029	0.033	0.066	0.176

* Time equals the mean renewal time. $E(N_t) = 1$.

related probability distributions may well apply, as in the instance of an electrode surface, where passivation occurs, in k distinct (mechanistic) stages, each having its time of duration $Y_1, Y_2, \ldots, Y_k$. If these times are independently distributed, each with an exponential PDF of $\rho \exp(-\rho y)$, then the onset of passivation occurs at a time $X = Y_1 + Y_2 + \ldots + Y_k$ and its PDF can be considered to be isomorphic to that of a Special Erlangian distribution (SED) where failure occurs at the end of the k-stage:

$$\text{p.d.f. (SED)} = \frac{\rho(\rho x)^{k-1} \exp(-\rho x)}{(k-1)!} \tag{10}$$

More generally, if each stage has an individual density ρ_i, $i = 1, \ldots, k$ the

$$\text{PDF (GED)} = \sum_{i=1}^{k} A_i \rho_i \exp(-\rho_i x) \tag{11}$$

$$A_i \equiv \prod_{j \neq i} \frac{\rho_j}{\rho_j - \rho_i} \tag{12}$$

characterises a General Erlangian distribution. These models of renewal theory could equally be utilised for the probabilistic description of multistage anodic dissolution and (cathodic) deposition processes under appropriate conditions.

The particular application presented in this paper is mathematically simple and serves as a precursor for a more complex employment of renewal theory, whose full scope remains to be explored.

6. Concluding remarks

The probabilistic approach based on equivalent models in renewal theory is an alternative to paths of analysis linked to modern stability theory and the theory of chaos. Both approaches offer interpretations which do not depend on the exact microscopic understanding of the physical process analysed, offering complementary tools for the study of physical phenomena.

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