

# Reliability models for electrochemical processes: some applications of the Weibull and Rayleigh probability distributions

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**Abstract** The potential usefulness of two important tools of reliability analysis: the Weibull and the Rayleigh distribution, is illustrated for three electrochemical processes, via cathode- and anode-failure, and deviations of alloy composition from target values. The examples show that (incorrectly assumed) normal and  $T$ -distribution can lead to serious numerical errors in estimating survival times.

**Keywords** Survival time · Electrode processes · Probability

## List of symbols

cdf	Cumulative distribution function
$D$	Kolmogorov–Smirnov–Lilliefors statistic
$E$	Expectation (expected value) of a random variable
$f(t)$	pdf of the random variable $T$
$F(t)$	cdf of the random variable $T$
$f_R(t)$	pdf of the Rayleigh distribution of $T$
$F_R(t)$	cdf of the Rayleigh distribution of $T$
$F_R(w)$	cdf of the Rayleigh distribution of $W$
$F_N(z)$	cdf of the standardized normal variate $Z$
$F(\chi^2; T; 2)$	cdf of the chi-square distribution of $T$ , with degree of freedom 2
$h(t)$	Failure rate function (or hazard rate function)
$i$	Position index
pdf	Probability density function
RA	Reliability analysis
$r$	Correlation coefficient
SL	Significance level

$T$	Random survival time; symbol for (Student's) $T$ -distribution
$t$	Numerical value of the random variable survival time $T$
$u$	“Dummy” integration variable
$w$	Numerical value of the random variable deviation norm $W$
$W$	Random variable deviation norm
$X, Y$	Independent random normal variables; $x, y$ their numerical values, respectively
$Z$	Random standardized normal variable; $z$ its numerical value

## Greek letters

$\alpha, \beta, \gamma, \theta$	Parameters of the Weibull and the Rayleigh distributions
$\eta, \sigma$	Standard deviation of a Rayleigh distribution
$\mu$	The mean (or expectation) of a Weibull or Rayleigh distribution
$\chi^2$	Random chi-square distribution variable

## 1 Introduction

Reliability can be defined as the probability that “... an entity will survive fully functional throughout a particular time-span ...” [1]. An entity may be a product, a process, a system, a subsystem of a complex structure, or any item serving a specific purpose or utility. Reliability analysis (RA) is at the core of system design and evaluation, and as such, it is an essential component of modern engineering. Time to failure (or simply, failure time), mean time between failures, and risk assessment are major concepts in RA.

There is at present, at least to the author's knowledge, little if any exploration of the utility of this subject area in the electrochemical engineering literature. The purpose of

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this paper, stemming from this paucity, is to provide an introductory treatment of certain electrochemically oriented reliability scenarios. Since *pertinent* quantitative information is not readily available, the numerical illustrations in Sect. 3 are based on hypothetical situations, which nonetheless indicate the nature of observations necessary for an (at least) adequate potential utilization of RA in the electrochemical domain.

## 2 Basic theory

As in any probabilistic approach, the fundamental tools of analysis are the probability density function (pdf)  $f(t)$ , and the cumulative distribution function (cdf)  $F(t)$  of failure time  $T$ , a continuous random variable. The relationship

$$F(t) = \int_0^t f(u)du \tag{1}$$

defines the probability  $P\{T \leq t\}$ , where  $t$  is an a-priori arbitrary time instant (from elementary probability theory,  $P\{T \leq t\} = P\{T < t\}$ , inasmuch as the probability  $P\{T = t\} = 0$ , due to the continuous nature of failure time). The complementary probability

$$P\{T > t\} = 1 - F(t) \tag{2}$$

known as the reliability function, or the survival function, yields the probability that an item survives past failure time  $T = t$ . The significance of the failure rate function (or hazard rate function), defined as

$$h(t) = \frac{f(t)}{1 - F(t)} \tag{3}$$

is manifested by  $h(t)dt$ , which is the approximate probability of failure in the  $(t, t + dt)$  interval, if it is known that an item has survived up to time  $t$ .

### 2.1 The Weibull distribution

Introduced nearly 70 years ago by a Swedish physicist whose name it is now bearing, the Weibull distribution has become a cornerstone tool of reliability analysis. Table 1 presents five differing pdf forms, where the unfortunate interchange of the  $\alpha, \beta$  parameters requires close attention.

**Table 1** Typical expressions for the probability density function of the Weibull distribution [for  $t < 0, f(t) = 0$ ]

Definition index	$f(t)$	Reference
1	$\frac{\beta}{\alpha} (\frac{t-\gamma}{\alpha})^{\beta-1} \exp(-(\frac{t-\gamma}{\alpha})^\beta)$	[2]
2	$\alpha\beta t^{\beta-1} \exp(-\alpha t^\beta)$	[3, 4]
3	$\alpha\beta^{-\alpha} t^{\alpha-1} \exp(-(\frac{t}{\beta})^\alpha)$	[5–7]
4	$\beta t^{\beta-1} \eta^{-\beta} \exp(-(\frac{t}{\eta})^\beta)$	[8]
5	$\gamma\theta^{-1} t^{\gamma-1} \exp(-\frac{t}{\theta})$	[9]

Definition 5 readily indicates that the transformed variable  $Y \equiv T^\gamma$  has the simple exponential distribution, with cdf

$$\begin{aligned} F_W(y) &= P\{Y \leq y\} = P\{T^\gamma \leq y\} = P\{T \leq y^{1/\gamma}\} \\ &= F_W\{y^{1/\gamma}\} = 1 - \exp\left[-y^{1/\gamma} \left(\frac{\gamma}{\theta}\right)\right] \\ &= 1 - \exp\left[-\frac{y}{\theta}\right] \end{aligned} \tag{4}$$

and yields the simple version of Eq. 3

$$h(t) = \frac{\gamma}{\theta} t^{\gamma-1} \tag{5}$$

indicating that the course of  $h(t)$  depends on the numerical value of the  $(\gamma - 1)$  exponent.

### 2.2 The Rayleigh distribution [2, 10]

Setting  $\alpha = 2$  and  $\beta = \sqrt{2}\eta$  in Definition 3 of Table 1, the Rayleigh distribution functions

$$f_R(t) = \eta^{-2} t \exp\left\{-\frac{1}{2} \left(\frac{t}{\eta}\right)^2\right\} \tag{6}$$

and

$$F_R(t) = 1 - \exp\left\{-\frac{1}{2} \left(\frac{t}{\eta}\right)^2\right\} \tag{7}$$

are obtained [11]. They were shown to be useful e.g. in software reliability [12], artillery communication theory [13, 14], and in the study of errors related to independently acting (transversal) accelerometers [11]. The latter application stems from a remarkable property of the distribution: if  $X$  and  $Y$  are independent normal random variables with zero mean and standard deviation  $\sigma$ , then their Euclidean norm (i.e. “radius”)  $\sqrt{(X^2 + Y^2)}$  possesses a Rayleigh distribution with  $\eta = \sigma$  and cdf

$$F_R(w) = 1 - \exp\left\{-\frac{1}{2} \left(\frac{w}{\eta}\right)^2\right\} \tag{8}$$

This relationship arises from the normal joint distribution function

$$f(x, y) = \frac{1}{2\pi\sigma^2} \exp\{-(x^2 + y^2)/2\sigma^2\} \tag{9}$$

upon an appropriate polar transformation [15]. Various properties of the Rayleigh distribution are also available on the Internet, e.g. [16, 17].

## 3 Potential applications to electrochemical processes

### 3.1 Weibull model-based analysis of failure time in a cathodic deposition process

A frequent shortcoming of steel cathodes used in certain chlor-alkali cells is an increase in their surface area,

leading to lower hydrogen overvoltage, hence a reduction in current efficiency [18, 19]. It is assumed that failure times in steel cathodes (claimed improved by a manufacturer), and due to mutually independent technical reasons, have been monitored in an experimental chlor-alkali cell. The 15 observations normalized with respect to an arbitrary reference time instant are in increasing order: 0.43; 0.51; 0.64; 0.72; 0.91; 0.98; 1.12; 1.19; 1.21; 1.22; 1.62; 1.72; 1.81; 2.32; 2.65

First, the validity of a Weibull model is established [20] by the  $Y_i \equiv \ln(16/(16-i))$  versus  $X_i \equiv \ln(t_i)$  plot in Fig. 1, with correlation coefficient  $r \approx 0.98$ . The parameters of the distribution are then estimated by solving simultaneously the relationships [21] pertaining to Definition 2 of Table 1:

$$\frac{\sum_{i=1}^{15} t_i^\beta \ln(t_i)}{\sum_{i=1}^{15} t_i^\beta} - \frac{1}{\beta} - \frac{\sum_{i=1}^{15} \ln(t_i)}{15} = 0 \tag{10}$$

and

$$\alpha = \frac{15}{\sum_{i=1}^{15} t_i^\beta} \tag{11}$$

for the pdf (repeated here for convenience)

$$f_R(t) = \alpha \beta t^{\beta-1} \exp(-\alpha t^\beta) \tag{12}$$

Accepting 0.007 as essentially zero on the right hand side of Eq. 10, the resulting parameter values  $\alpha = 0.4463$  and  $\beta = 2.2$  yield the cdf

$$F_R(t) = 1 - \exp(-0.4463t^{2.2}) \tag{13}$$

i.e. the probability that a deposition process would not fail within a dimensionless operation time period  $0 \leq T \leq t$ . The sample mean 1.27 and sample variance 0.4182 provide an unbiased estimate [22] of the population mean

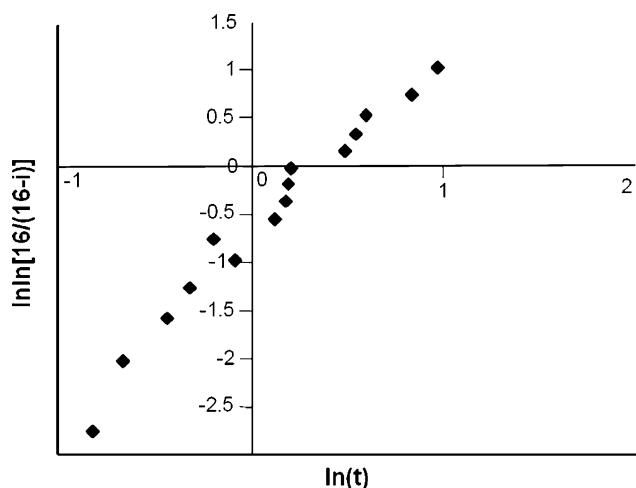


Fig. 1 Graphical test for the validity of the Weibull distribution in Sect. 3.1

$$\mu = \alpha^{-1/\beta} \Gamma\left(1 + \frac{1}{\beta}\right) = 1.278 \tag{14}$$

and population variance

$$\sigma^2 = \alpha^{-2/\beta} \left\{ \Gamma\left(1 + \frac{2}{\beta}\right) - \left[ \Gamma\left(1 + \frac{1}{\beta}\right) \right]^2 \right\} = 0.377 \tag{15}$$

### 3.2 Rayleigh model-based analysis of anode survival times

Magnetite anodes with closely controlled equi-molar ratios of the FeO and Fe<sub>2</sub>O<sub>3</sub> species have been shown to possess good stability in dilute chloride electrolytes containing alkali metals, and in chlorate cells [23, 24]. In a novel, but still experimental chlorate cell, nine magnetite anodes are assumed to have exhibited the following normalized survival times, in increasing order: 0.62; 0.74; 0.94; 1.07; 1.25; 1.41; 1.68; 1.82; 2.17. As in Sect. 3.1, the failures are mutually independent, and the manufacturing and the operating conditions of the anodes in the available stock have been closely controlled. Fig. 2, established by the procedure shown in Sect. 3.1, indicates that the Weibull model with  $r \approx 0.99$  is acceptable, yielding the cdf

$$F_R(t) = 1 - \exp(-t^2/2) \tag{16}$$

The results can, therefore, be interpreted in terms of a Rayleigh distribution, where the sample-based maximum likelihood [25] estimate of the variance

$$b^2 = \frac{\sum_{i=1}^9 t_i^2}{2n} = \frac{17.3548}{18} = 0.9641 \tag{17}$$

indicates that the adoption of  $\eta = 1$  (instead of  $b = 0.9819$ ) is quite reasonable. Since a Rayleigh distribution with  $\eta = 1$  is equivalent to a chi-square distribution with degree of freedom  $\nu = 2$  [10], the probability of survival time to  $T = t$  can also be computed from tables of the  $\chi^2$ -distribution

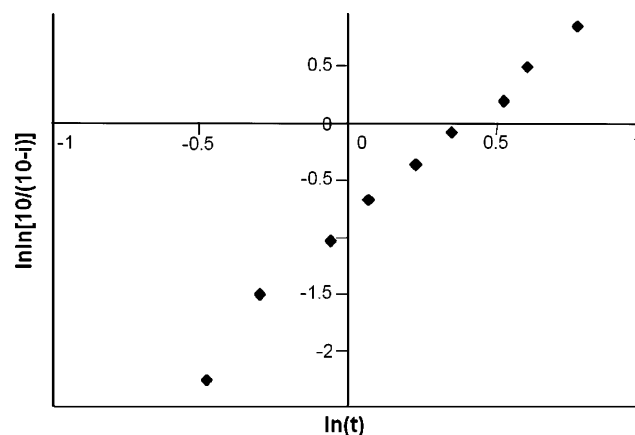


Fig. 2 Graphical test for the validity of the Weibull distribution (Rayleigh version) in Sect. 3.2

function [26]  $F(\chi^2; t^2; 2)$ . The sample mean of 1.3 and the sample variance of 0.2681 provide an unbiased estimate [10] of the population mean

$$\mu = \sqrt{\pi/2} = 1.253 \quad (18)$$

and population variance

$$\sigma^2 = \frac{4 - \pi}{2} = 0.429 \quad (19)$$

### 3.3 Rayleigh model-based analysis of electrodeposited alloy composition

The electrolytic deposition of Ni–Fe alloys has been the subject of intensive research for several decades. Relatively recent studies involving  $\text{NiSO}_4/\text{FeSO}_4$  and  $\text{NiSO}_4/\text{FeSO}_4/\text{H}_3\text{BO}_3$  electrolytes in RDE systems [27, 28] provide electrokinetic parameters (transfer coefficient and surface rate constant) for the direct  $\text{Ni(II)} \rightarrow \text{Ni}$  and  $\text{Fe(II)} \rightarrow \text{Fe}$  reduction reactions. Magnetic field imposition has been shown [29] to increase the Fe content of the alloy deposited from a modified Watt's bath. A conventional target composition [30] of 80% Ni–20% Fe, to be achieved in a cell of this kind, is specified to illustrate the usefulness of the Rayleigh distribution. The analysis concerns the two-dimensional composition state vector  $(x; y)$  comprised of deviations from the target values  $[\text{Ni}] = 80\%$  and  $[\text{Fe}] = 20\%$ , respectively. The norm of the state vector  $w = \sqrt{x^2 + y^2}$  is a Rayleigh variate if the vector elements  $x$  and  $y$  are normally distributed, and independent with zero mean and standard deviation  $\eta$  (Sect. 2.2). The geometric interpretation considers the vector norm as the radius of the circle with centre at  $(0,0)$ , where  $x = 0$  corresponds to 80% Ni and  $y = 0$  corresponds to 20% Fe. (From a purely set-theoretic point of view,  $w$  is also the square root of the inner product of vector elements  $x$  and  $y$ ).

It is assumed that 10 randomly selected alloy deposit samples yield the following observations arranged in increasing order:

$X$ : {−2.47; −0.88; −0.58; −0.021; 0.028; 0.19; 0.63; 0.83; 0.93; 1.43}; mean = 0.087; variance = 1.2493  
 $Y$ : {−2.23; −1.41; −0.43; −0.20; −0.10; 0.62; 0.62; 0.94; 1.02; 1.18}; mean = 0.001; variance = 1.2535

In order to ascertain whether the two distributions can be considered to be normal, the Lilliefors modification of the Kolmogorov–Smirnov test [31–33], described briefly in the Appendix, is employed. Since the magnitudes of  $D_{\max} = 0.1267$  for the  $X$ -set, and 0.147 for the  $Y$ -set are well below the 5% critical value of 0.258, the test fails to reject the a-priori (or null) hypothesis of normal distribution, hence the Rayleigh-model is admissible. Accordingly, the numerical form of Eq. 8

$$F_R(w) \cong 1 - \exp\left(-\frac{1}{2}\left(\frac{w}{1.12}\right)^2\right) = 1 - \exp(-0.4w^2) \quad (20)$$

yields  $P[W \leq w]$ , i.e. the probability that the deviation norm will not exceed the value  $w$ , where  $W$  is the random deviation-norm variable. With  $\eta = 1.12$  (i.e. by rounding the two nearly equal standard deviations  $\sqrt{1.2493} = 1.1177$  and  $\sqrt{1.2535} = 1.1195$ ), the population mean and standard deviation are computed [33] to be

$$\mu_w = \eta\sqrt{\frac{\pi}{2}} = 1.404$$

$$\sigma_w = \eta\sqrt{\frac{4 - \pi}{2}} = 0.733$$

respectively.

## 4 Analysis of results and discussion

Process analysts are frequently interested in the fraction of observations that may be expected to fall between the population mean plus  $k$ -times the standard deviation, where  $k$  is an integer, typically from  $-4$  to  $+4$ . For cathode survival in Sect. 3.1, comparison of the Weibull, the standard normal and the approximately normal  $T$ -distribution in Table 2 demonstrates that the latter two (if used by oversight, or by ignorance of Weibull distribution theory) would yield discernibly different estimates. If only cathodes exhibiting survival times larger than the reference time were declared acceptable, all three models would predict essentially the same fraction (Weibull: 0.64;  $Z$  and  $T$ : 0.66) of such cathodes. Similar conclusions may be drawn from Table 3 for rejection of cathodes with survival times below the reference time.

In the anode survival case (Sect. 3.2) the in principle erroneous application of  $Z$ - and/or  $T$ -distribution would

**Table 2** Estimates of the fraction of cathode survival times in Sect. 3.1 via the Weibull, standard normal, and the  $T$ -distribution

Interval	Fraction of estimated survival times		
	Weibull <sup>a</sup>	Normal <sup>b</sup>	$T$ <sup>c</sup>
$(\mu - \sigma) - (\mu + \sigma)$	0.6467	0.6826	0.6658
$(\mu - 2\sigma)^d - (\mu + 2\sigma)$	0.9467	0.9544	0.9348

<sup>a</sup>  $\mu_w = 1.278$ ;  $\sigma_w^2 = 0.377$

<sup>b</sup> The sample mean 1.27 and sample variance 0.4182, unbiased estimates of the population mean and variance, respectively, were used to compute the  $Z$ - and  $T$ -scores

<sup>c</sup> Computed via  $T$ -distribution tables [34] with  $\{v\} = 14$  degrees of freedom

<sup>d</sup> Set to zero, as a reasonable approximation to  $1.27 - 2\sqrt{0.4182} = -0.0234$

**Table 3** Estimates of the fraction of rejected cathodes in Sect. 3.1 via the Weibull, standard normal, and *T*-distribution

Dimensionless survival time	Expected fraction of rejected cathodes		
	Weibull	Normal	<i>T</i> <sup>a</sup>
≤0.5	0.110	0.117	0.127
≤0.7	0.196	0.189	0.197
≤0.9	0.248	0.233	0.239

<sup>a</sup> Computed via *T*-distribution tables [34] with  $\nu = 14$  degrees of freedom

**Table 4** Estimates of the fraction of anode survival times in Sect. 3.2 via the Rayleigh, the chi-square, the normal, and the *T*-distribution

Interval	Fraction of estimated survival times			
	Rayleigh <sup>a</sup>	Chi-square <sup>b</sup>	Normal <sup>c</sup>	<i>T</i> <sup>d</sup>
$(\mu - \sigma) - (\mu + \sigma)$	0.5448	0.5452	0.6826	0.6564
$(\mu - 2\sigma) - (\mu + 2\sigma)$	0.9002	0.9005	0.9544	0.9194

<sup>a</sup>  $\mu_R = 1.2533$ ;  $\sigma_R^2 = 0.4392$

<sup>b</sup> Computed via chi-square distribution tables [21] with  $\nu = 2$  degrees of freedom

<sup>c</sup> The sample mean 1.3 and sample variance 0.2681, unbiased estimators of the population mean and population variance, respectively, were used to compute the *Z*- and *T*-scores

<sup>d</sup> Computed via *T*-distribution function tables [34] with  $\nu = 8$  degrees of freedom

yield larger numerical discrepancies, as seen in Tables 4 and 5. The small disagreements shown by the chi-square estimates with respect to the Rayleigh distribution are due to linear interpolation between tabulated values of the chi-square cdf [26].

The failure rate functions

$$h(t) = 0.982t^{1.2} \tag{21}$$

for cathode survival, and

$$h(t) = t \tag{22}$$

for anode survival portray the tendency of the differential probability to increase with the length of survival time. The linearity of the survival function with respect to time, obtained by substituting Eqs. 6 and 7 into Eq. 3, is a distinct characteristic of the Rayleigh distribution.

The importance of using the right distribution hinges on the severity of acceptance. If, for instance, up to one quarter of the experimental cathodes were allowed to have a less than 0.9 dimensionless survival time, the Weibull distribution in Table 3 would indicate to the analyst that some modifications in cathode preparation would be warranted, since the expected fraction of 0.248 is very close to the stipulated value of 1/4. The *Z*- and *T*-distribution, however, would fail to question the properness of the cathode preparation process. Similarly, if at least 35% of the anodes were stipulated

**Table 5** Estimates of the fraction of acceptable anodes in Sect. 3.2 via the Rayleigh, the chi-square, the normal, and the *T*-distribution

Dimensionless survival time	Expected fraction of acceptable anodes			
	Rayleigh	Chi-square	Normal	<i>T</i>
≥1.0	0.6065	0.6065	0.6517	0.6466
≥1.5	0.3246	0.3248	0.3520	0.3671
≥2.0	0.1353	0.1353	0.1271	0.1439

to possess a dimensionless survival time 1.5 or larger, the Rayleigh (and chi-square) distribution in Table 5 would indicate a defective anode behaviour on the whole, but the *Z*- and *T*-distribution would make the erroneous impression that the anodes are acceptable.

The cdf of the Rayleigh distribution in Sect. 3.3 (Eq. 20) provides the probability of a specified deviation from target composition, when it is immaterial for the process analyst to what extent the stated deviation magnitude is made up by the two metals. In other words, the individual magnitudes of *x* and *y* are of no specific interest as long as  $w = \sqrt{x^2 + y^2}$  remains a specified constant. If, on the other hand, the analyst is interested in the probability of individual deviations, joint probability distributions are needed for analysis. In the illustration of Sect. 3.3, the probability e.g. that deviations from target composition will not exceed  $x_1\%$  Ni and  $y_1\%$  Fe in magnitude, is given by

$$\begin{aligned}
 P[0 \leq X \leq x_1; 0 \leq Y \leq y_1] &= \left\{ \frac{1}{\sqrt{2\pi}} \int_0^{x_1/1.12} \exp(-u^2) du \right\} \\
 &\times \left\{ \frac{1}{\sqrt{2\pi}} \int_0^{y_1/1.12} \exp(-u^2) du \right\} \\
 &= \left[ F_N\left(\frac{x_1}{1.12}\right) - \frac{1}{2} \right] \left[ F_N\left(\frac{y_1}{1.12}\right) - \frac{1}{2} \right] \tag{23}
 \end{aligned}$$

with the standard normal cdf

$$F_N(z) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^z \exp\left(-\frac{u^2}{2}\right) du \tag{24}$$

Table 6 shows clearly that the Rayleigh distribution-based probabilities are considerably larger than the joint normal distribution-based probabilities, inasmuch as a given numerical value of  $w = w_1$  encompasses all *x* and *y* values obeying the  $w_1 = \sqrt{x^2 + y^2}$  relationship.

At very small survival times, the Weibull and the Rayleigh cdf's can be approximated at a reasonable accuracy by the positive argument of their exponential functions. Thus, Eqs. 13 and 20 can be replaced by

$$F_R(t) \cong 0.4463t^{2.2}; \quad -0.35 \leq t \leq 0.35 \tag{25}$$

and

**Table 6** Selected probabilities of per cent deviation magnitudes of Ni and Fe from the target composition in Sect. 3.3

Definition of probability	Expression	Numerical value of probability
$P[W \leq 1]$	$F_W(1) = 1 - \exp(-\frac{1}{2}(\frac{1}{1.12})^2)$	0.3287
$P[ x  \leq 0.5;  y  \leq 0.866]$ $w = \sqrt{x^2 + y^2} \leq 1$	$[F_N(\frac{0.5}{1.12}) - \frac{1}{2}][F_N(\frac{0.866}{1.12}) - \frac{1}{2}]$	0.049
$P[ x  \leq 0.3;  y  \leq 0.954]$ $w = \sqrt{x^2 + y^2} \leq 1$	$[F_N(\frac{0.30}{1.12}) - \frac{1}{2}][F_N(\frac{0.954}{1.12}) - \frac{1}{2}]$	0.032
$P[W \geq 2]$	$1 - F_W(2) = \exp(-\frac{1}{2}(\frac{2}{1.12})^2)$	0.203
$P[ x  \geq \sqrt{2};  y  \geq \sqrt{2}]$ $w = \sqrt{x^2 + y^2} \geq 2$	$[1 - F_N(\frac{\sqrt{2}}{1.12})][1 - F_N(\frac{\sqrt{2}}{1.12})]$	0.011
$P[ x  \geq 1.6;  y  \geq 1.2]$ $w = \sqrt{x^2 + y^2} \geq 2$	$[1 - F_N(\frac{1.6}{1.12})][1 - F_N(\frac{1.2}{1.12})]$	0.011
$P[0.1 \leq w \leq 0.2]$	$F_W(0.2) - F_W(0.1) = \exp(-\frac{1}{2}(\frac{0.1}{1.12})^2) - \exp(-\frac{1}{2}(\frac{0.2}{1.12})^2)$	0.012
$P[w_1 \leq w \leq w_2]$ $w_1 = \sqrt{0.09^2 + 0.0436^2} = 0.1$ $w_2 = \sqrt{0.09^2 + 0.179^2} = 0.2$	$[F_N(\frac{0.09}{1.12}) - \frac{1}{2}][F_N(\frac{0.179}{1.12}) - \frac{1}{2}] - [F_N(\frac{0.09}{1.12}) - \frac{1}{2}][F_N(\frac{0.0436}{1.12}) - \frac{1}{2}]$	$5 \times 10^{-4}$

$$F_R(w) \cong 0.4w^2; \quad -0.35 \leq w \leq 0.35 \quad (26)$$

respectively, at a relative error smaller than about  $-2\%$ .

Finally, Eqs. 16 and 20 imply that a Rayleigh distribution can also be considered as an exponential distribution with variates  $t^2$  and  $w^2$ , and with parameters 2 and 0.4, respectively, as a special case of Eq. 4.

## 5 Final remarks

In a world increasingly conscious of environmental issues and conservation, the design and operation of equipment with large survival times will be a challenging goal for new and modified electrochemical technologies. The techniques of applied probability theory presented here will be among the important tools for motivated electrochemists and electrochemical engineers.

Survival function analysis is not limited to random variables with known probability distributions. Discussion of appropriate methods (e.g. the Kaplan–Meier technique [35]) of nonparametric statistics for estimating survival times is, however, beyond the scope of this paper.

## Appendix

### A brief summary of the Lilliefors test for normality

Let the set  $x_1, x_2, \dots, x_n$  be a sample of random observations taken from a population with unknown mean and variance, arranged in increasing order, with sample mean  $\bar{x}$  and sample variance  $s^2$ . From the set of absolute values of the difference variable

$$D_i = F_N\left(\frac{x_i - \bar{x}}{\sqrt{s^2}}\right) - \frac{i}{n} \quad (A.1)$$

the largest value  $|D_i|_{\max}$  is compared to tabulated critical values [31, 32, 36] at various significance levels  $\alpha$  (5%: significant level; 1%: highly significant level). If at a chosen significance level  $|D_i|_{\max}$  is less than the critical value, normality of the data may be assumed.

For the observation sets in Sect. 3.3, the critical values at  $n = 10$  are: 0.215 (SL = 20%); 0.224 (15%); 0.239 (10%); 0.258 (5%), and 0.294 (1%). For  $n > 30$ , the critical value is  $C/\sqrt{n}$ , where the constant  $C$  is determined by the chosen SL.

The Lilliefors test is a modification of the Kolmogorov–Smirnov test, the latter applicable in exactly the same manner when the population mean and population variance are known. The critical values, however, are different in the two tests [if in Sect. 3.3 the mean and variance were population parameters, the K–S critical values to use would be 0.266 (SL = 20%); 0.283 (15%); 0.304 (10%); 0.338 (5%); 0.404 (1%)].

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