JOURNAL OF APPLIED ELECTROCHEMISTRY **20** (1990) 901-906

An analysis of random perturbations in electrolyzers

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Received 5 February 1990; revised 27 March 1990

A method of analysis of the stochastic behaviour of electrolyzers due to stationary random fluctuations in current and inlet electrolyte concentration is presented. The analysis is illustrated by means of a numerical example.

Nomenclature

c	electrolyte concentration; c_I inlet electrolyte concentration; c_E exit electrolyte concentration (mol dm^{-3})
F	Faraday's constant (96 487 C mol^{-1})
I	current (A)
j	imaginary unit $= \sqrt{(-1)}$
K	equivalent gain
$N(A)$	nonlinear function of amplitude A of an independent variable
n	number of electrons participating in the electrode process
$P(z)$	probability density function of random variable z
Q	electrolyte volumetric flow rate (dm^3 min^{-1})
$R_z(\lambda)$	autocorrelation function
$S_z(\omega)$	power spectrum of random variable z
T_0, T_1	Frequency characteristic parameters (obtained from process reaction curve)
u	shorthand for the product αz_1 (see Equation 30)
V	active volume of electrolyzer (dm^3)
v	shorthand for the product βz_2 (see Equation 30)
x	dimensionless exit electrolyte concentration
z_1	dimensionless electrolyte inlet concentration
z_2	dimensionless current
α	lumped parameter defined as $-c_I^*/c_E^*$
β	lumped parameter defined as $I^*/nFQc_E^*$
γ	lumped parameter defined as a $I^*/nFVc_E^*$
λ	'dummy' integration variable
σ_z^2	variance (or mean power) of random variable z
τ	mean residence time in electrolyzer, equal to V/Q (min)
$\phi(j\omega)$	frequency spectrum
ω	angular frequency

Special symbols and functions

*	steady state (superscript)
erf	error function, defined as $\mathrm{erf}\,(z) = \frac{2}{\sqrt{\pi}} \int_0^z \exp\,(-\lambda^2)\,\mathrm{d}\lambda$
o	step magnitude (superscript)
H	Heaviside's shifting function, defined as $H(t-\tau) = 0$ for $t < \tau$; $H(t-\tau) = 1$ for $t \geqslant \tau$
Γ	gamma function, defined as $\Gamma(z) = \int_0^\infty \lambda^{z-1} \exp\,(-\lambda)\,\mathrm{d}\lambda$
CSTER	acronym for continuous flow stirred tank electrolytic reactor
PFER	acronym for plug-flow electrolytic reactor

1. Introduction

Random perturbations in physical systems are usually caused by unexpected changes in parameters or operating conditions, faulty components and connections and by human error. Such perturbations are treated more efficiently by techniques of probability theory than by deterministic mathematical methods, provided that their stochastic characteristics are known. A particularly interesting and useful domain of the random perturbation approach is process dynamics and control, with a well-established fundamental theory (for example [1-7]), permitting the estimation of the behaviour of system output on the basis of the stochastic parameters of input(s), and the dynamic characteristics of the system itself.

The treatment of random perturbations in electrolytic reactors has so far received limited attention [8-11], due to inherent difficulties in treating non-ideal electrolyzer dynamics (i.e., the dynamics of electrolyzers *not* amenable to the CSTER or PFER approach). The major utility of the stochastic approach lies in the determination of electrolyzer performances from 'on-line' information obtained from recorded plant data: it is not necessary to subject an electrolyzer to off-line, purposefully induced perturbations. Information thus obtained without the interruption of normal (day-to-day) operation schedules can be employed to predict electrolyzer performance under various stochastic conditions and it can serve as a tool for design of control as well as analysis.

The approach described in this paper addresses a specific avenue of stochastic analysis, where the variance of output behaviour is used as a measure of performance. The exact form of the random perturbations in the input is immaterial so long as their

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stochastic properties (e.g. correlation functions) are known. The approach applies in principle to any arbitrary electrolyzer, regardless of its size, shape, geometry and electrode type, although specific simplifications may be feasible in particular configurations.

2. Basic theory

Consider an arbitrary electrolyzer with stationary random perturbations in the electric current (single-perturbation), or in the electric current and the inlet electrolyte concentration (dual perturbation). The output perturbation is taken to be the stochastic response of the effluent electrolyte concentration. This assumption appears to confine the approach to electrolyzers where outlet concentration may be regarded as a reliable measure of electrolyzer performance, but other outputs can also be accommodated, if necessary. The outlet electrolyte concentration, a convenient variable to monitor continuously, is in any event a desirable choice. It is assumed that the perturbations in electric current and inlet electrolyte concentration are mutually independent, i.e. that their cross-correlation function is zero. The dynamics of the electrolyzer is represented by the product of two functions. The first function, known as the frequency spectrum, is obtained from experimental transient response data, and the second function, which expresses the effect of input perturbation amplitudes on the response, represents nonlinearities. In this manner the dynamics are represented by the product of a linear, purely frequency-dependent function, and a nonlinear, purely amplitude-dependent function. This is also the fundamental idea in the classical 'describing function' approach [6, 7, 12] to nonlinear system stability, whose applicability to a certain class of electrolyzers has been discussed [13] earlier. Then, in the case of a single perturbation, the response variance is given by the integral

$$\sigma_x^2 = \int_{-\infty}^{+\infty} N^2(A)|\phi(\mathrm{j}\omega)|^2 \, S_z(\omega) \, \mathrm{d}\omega \qquad (1)$$

where the dimensionless input and output variables are defined as

$$z \equiv (I - I^*)/I^* \text{ and } x \equiv (c^* - c)/c^* \qquad (2)$$

the asterisk referring to the state of the electrolyzer prior to perturbation. The variance of the input perturbation is given by the similar expression

$$\sigma_z^2 = \int_{-\infty}^{+\infty} S_z(\omega) \, \mathrm{d}\omega \qquad (3)$$

The power spectrum $S_z(\omega)$ is the Fourier transform of the input autocorrelation function $R_z(\lambda)$:

$$S_z(\omega) = \int_{-\infty}^{+\infty} R_z(\lambda) \exp(-\mathrm{j}\omega\lambda) \, \mathrm{d}\lambda \qquad (4)$$

In the case of a dual perturbation (perturbation in current and inlet concentration), the dimensionless input variables are defined as

$$z_1 \equiv (c_i - c_i^*)/c_i^* \qquad (5a)$$

$$z_2 \equiv (I - I^*)/I^* \qquad (5b)$$

Equations 3 and 4 define the stochastic characteristics of the two input perturbations required for treatment in the sequel. In order to obtain σ_x^2, $N(A)$ and $\phi(\mathrm{j}\omega)$ must be established; a particular approach to this task is via the equivalent gain and the process reaction curve.

3. Treatment of the perturbation amplitude effect: the equivalent gain approach

The equivalent gain principle is a linear approximation to a nonlinear function when the independent (or input) variable is a stationary random function [7, 8, 14]. The equivalent gain is obtained by minimizing the residual in the conventional least-squares sense, and it can be written as

$$K = \frac{1}{\sigma_z^2} \int_{+\infty}^{+\infty} z \, \mathrm{f}(z) \mathrm{P}(z) \, \mathrm{d}z \qquad (6)$$

where f(z) is the mathematical expression for the nonlinearity. If, in particular, the random perturbation in the input is Gaussian with probability density function

$$\mathrm{P}(z) = \frac{1}{\sigma_z \sqrt{(2\pi)}} \exp(-z^2/2\sigma_z^2) \qquad (7)$$

then the equivalent gain is simplified to

$$K = \frac{1}{\sigma_z \sqrt{(2\pi)}} \int_{-\infty}^{+\infty} \frac{\mathrm{df}(z)}{\mathrm{d}z} \exp(-z^2/2\sigma_z^2) \, \mathrm{d}z \qquad (8)$$

Modification of Equation 8 for two independent Gaussian inputs simply requires the replacement of σ_z^2 by the sum of the individual variances. It follows that the quantity K, computed via Equations 6 or 8, replaces $N(A)$ in Equation 1; this is an important simplification.

4. Treatment of the frequency spectrum: the process reaction curve approach

The process reaction curve approach is a convenient means of establishing the frequency spectrum of a system from the experimental response to a step perturbation in the input [15]. In one of its modern and more accurate version by Smith [16, 17], a frequency spectrum of the form

$$\phi(\mathrm{j}\omega) = \exp(-\mathrm{j}T_0\omega)/(1 + \mathrm{j}T_1\omega) \qquad (9)$$

is obtained by measuring θ_1, the time required for the experimental response to reach 28.3% and θ_2, the time required to reach 63.2 of the overall change. Then, $T_1 = 1.5(\theta_2 - \theta_1)$ and $T_0 = \theta_2 - T_1$ are calculated. In the Ziegler-Nichols [15, 17] approach a tangent line is drawn at the inflection point of the process reaction curve, whose intersection with the time axis is the assigned delay-time parameter in the exponential term of Equation 9. The time constant is obtained by subtracting this intersection value from the intersection of the large-time asymptote and the tangent line, projected on the time axis. While this method is faster, it may assign an unduly large delay time if the process response is not sluggish at very short times. The first-order form of $\phi(\mathrm{j}\omega)$ in Equation 9 is quite acceptable for a single electrolyzer, although second-order construction methods [18, 19] are also available if the electrolyzer response is too sluggish for a first-order approximation. $\phi(\mathrm{j}\omega)$ may also be regarded as the transfer function of the electrolyzer, obtained by Fourier transformation of its time-domain dynamic equation. The latter is not *a priori* solvable, of course, in the case of an (arbitrary) non-ideal electrolyzer.

5. The non-ideal tank electrolyzer

It follows from the overall material balance (assuming 100% current efficiency):

$$V\,\mathrm{d}c/\mathrm{d}t = Qc_{\mathrm{i}} - Qc_{\mathrm{E}} - I/nF \qquad (10)$$

that the steady-state dimensionless exit concentration, inlet concentration and current are related by the linear expression

$$x = \alpha z_1 + \beta z_2 \qquad (11)$$

which serves for the determination of $N(A)$ or K, if the equivalent gain approach is chosen. Let the superscripted values z_i' and z_i'', i = 1, 2, denote the lower and upper bounds, respectively, of perturbation magnitudes; these bounds are dictated by technological considerations for a given electrolytic process. In the instance of perturbation in the current ($z_1 = 0$) Equation 7 takes the form of

$$K = \beta/2\,[\mathrm{erf}\,(1/\,\hat{\sigma}_2) + \mathrm{erf}\,(1/\hat{\sigma}_1)] \qquad (12)$$

where

$$\hat{\sigma}_2 \equiv \frac{\sqrt{2}}{|z_2''|}\,\sigma_{z_2} \qquad (13\mathrm{a})$$

and

$$\hat{\sigma}_1 \equiv \frac{\sqrt{2}}{|z_2'|}\,\sigma_{z_2} \qquad (13\mathrm{b})$$

are dimensionless standard deviations related to the standard deviation of the current fluctuation. In the case of dual perturbation

$$K = 1/2\,[\mathrm{erf}\,(1/\hat{\sigma}_2) + \mathrm{erf}\,(1/\hat{\sigma}_1)] \qquad (14)$$

where the dimensionless composite standard deviations are defined as

$$\hat{\sigma}_2 \equiv \frac{\sqrt{(2(\alpha^2\sigma_{z_1}^2 + \beta^2\sigma_{z_2}^2))}}{|\alpha z_1'' + \beta z_2''|} \qquad (15\mathrm{a})$$

and

$$\hat{\sigma}_1 \equiv \frac{\sqrt{(2(\alpha^2\sigma_{z_1}^2 + \beta^2\sigma_{z_2}^2))}}{|\alpha z_1' + \beta z_2'|} \qquad (15\mathrm{b})$$

The determination of the frequency spectrum from the process reaction curve is illustrated numerically in Section 7.

6. Electrolyzers possessing deterministic models

The CSTER, the PFER, and electrolyzers with axial dispersion are considered in this category. Since $c = c_{\mathrm{E}}$ at any instant in a CSTER by its definition, Equation 16 follows directly from the solution of Equation 10 under a step perturbation in current as well as in inlet concentration:

$$x = (\alpha z_1^0 + \beta z_2^0)\,[1 - \exp\,(-t/\tau)] \qquad (16)$$

The equivalent gain is given by Equations 12 or 14, whereas the frequency spectrum can be expressed as

$$\phi(\mathrm{j}\omega) = \frac{1}{1 + \mathrm{j}\tau\omega} \qquad (17)$$

Consequently, the variance of the exit concentration (Equation 1) acquires the relatively simple expression

$$\sigma_x^2 = K^2 \int_{-\infty}^{+\infty} \frac{S_z(\omega)}{1 + \tau^2\omega^2}\,\mathrm{d}\omega \qquad (18)$$

In the case of a PFER, the dynamic material balance [20]

$$\frac{\partial c}{\partial t} + v\frac{\partial c}{\partial y} + \frac{I}{zFV} = 0 \qquad (19)$$

possesses an analytical solution only if the *a priori* space-dependent current is replaced by a mean value I_{m}, in which case the solution of Equation 19 (dual step perturbations):

$$x = \alpha H(t - \tau)z_1^0 + \beta\,[t/\tau - (t/\tau - 1)\,H(t - \tau)]\,z_2^0 \qquad (20)$$

indicates that the PFER has two separate frequency spectrum components:

$$\phi_1(\mathrm{j}\omega) = \gamma\,\frac{1 - \exp\,(-\mathrm{j}\tau\omega)}{\omega} \qquad (21\mathrm{a})$$

and

$$\phi_2(\mathrm{j}\omega) = \exp\,(-\mathrm{j}\tau\omega) \qquad (21\mathrm{b})$$

Consequently, the output variance becomes

$$\sigma_x^2 = K_1^2 \int_{-\infty}^{\infty} S_{z_1}(\omega)\,\mathrm{d}\omega + 4K_2^2 \int_{-\infty}^{+\infty} \frac{\sin^2\,(\tau\omega)}{\omega^2}\,S_{z_2}(\omega)\,\mathrm{d}\omega \qquad (22)$$

Finally, in the case of an electrolyzer with axial dispersion, further manipulation (of Equations 6 and 13 in [21]) yields

$$x = \alpha(1 - Y_t)\,z_1 + \beta z_2 \qquad (23)$$

where Y_t (the multiplier in the last term on the right hand side of Equation 13 [21] at the electrolyzer exit) represents the effect of axial dispersion. Since Y_t approaches zero at large times, the equivalent gains remain unchanged, but the frequency spectrum related to dual perturbation acquires the form

$$\phi(\mathrm{j}\omega) = a + b\,\frac{\exp\,(-\mathrm{j}T_0\omega)}{1 + \mathrm{j}T_1\omega} \qquad (24)$$

where

$$a \equiv x_0/\mathrm{x}_\infty \qquad (25\mathrm{a})$$

and

$$b \equiv (x_\infty - x_0)/x_\infty \tag{25b}$$

The time constants T_0 and T_1 are obtained from a process reaction curve in the usual manner, but it is convenient to plot the dimensionless transient response $(x - x_0)/(x_{00} - x_0)$ against time. If $T_0 \ll T_1$ then Equation 24 is simplified to a rational expression and it follows that

$$\sigma_x^2 = K_1^2 \int_{-\infty}^{+\infty} \frac{(b+a)^2 + T_1^2 a^2 \omega^2}{1 + T_1^2\omega^2} S_{z_1}(\omega)\, d\omega + K_2^2 \int_{-\infty}^{+\infty} S_{z_2}(\omega)\, d\omega \tag{26}$$

7. Numerical illustration

An arbitrary electrolyzer with numerical parameters given in Table 1 is subjected to stationary random perturbations. In the case of a single perturbation, the autocorrelation function of the current is assumed to have been determined by conventional methods, for example [1], as

$$R_{z_2}(\tau) = a_2 \exp(-b_2|\tau|) \tag{27}$$

and, in the case of dual perturbation, it is assumed that the current has the same autocorrelation function, while the inlet concentration has

$$R_{z_1}(\tau) = a_1 \exp(-b_1\tau^2) \tag{28}$$

as its autocorrelation function, with numerical values shown in Table 1.

7.1. *Single perturbation*

The experimental transient response of the electrolyzer to a low-amplitude (0.5 A) step perturbation in current (postulated for the sake of illustration) is shown in Fig. 1. The Smith construction technique applied to the x/x_∞ against time plot yields $T_0 = 4.375$ and $T_1 = 13.125$ min (the Ziegler-Nichols approach yields the less reliable values of $T_0 = 6$ and $T_1 = 5.875$ min).

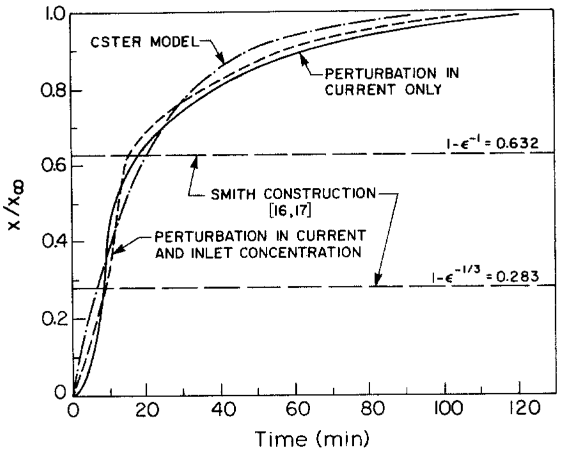

Fig. 1. Low-amplitude step perturbation response in the arbitrary electrolyzer [$\Delta I = 0.5$ A, $\Delta c_i = -10^{-4}$ mol dm^{-3}].

Table 1. Parameters of the arbitrary electrolyzer in the numerical illustration (assumed values)

Active electrolyzer volume	$V = 100\,\text{dm}^3$
Volumetric electrolyte flow rate	$Q = 5\,\text{dm}^3\,\text{min}^{-1}$
Number of electrons transferred in electrode reaction of interest	$n = 2$
Current prior to perturbation	$I^* = 10$ A
Inlet concentration prior to perturbation	$c_i^* = 0.001\,\text{mol dm}^{-3}$
Exit concentration prior to perturbation	$c_E^* = 3.782 \times 10^{-4}\,\text{mol dm}^{-3}$
Lumped operation parameters	$\alpha = -c_i^*/c^* = -2.6441$ $\beta = I^*/QnFc_E^* = 1.6441$
Parameters of correlation functions	$a_1 = 0.09$ $a_2 = 0.15$ $b_1 = 0.4$ $b_2 = 1.0$
Boundaries of input perturbations (in terms of dimensionless variables):	
Lower	$z_1' = -0.3$ $z_2' = -0.2$
Upper	$z_1'' = 0.6$ $z_2'' = 0.4$

Equation 4 yields $S_{z_2}(\omega) = 0.3/(1 + \omega^2)$ and from Equation 3, $\sigma_{z_2}^2 = 0.9425$. Since, from Equation 13, $\hat{\sigma}_1 = 6.8647$ and $\hat{\sigma}_2 = 3.4323$, it follows from Equation 12 that $K = 0.3970$. Finally, Equation 1 is integrated [22]

$$\sigma_x^2 = 0.0946 \int_0^\infty \frac{d\omega}{(1+\omega^2)(1 + 172.266\,\omega^2)} = 0.011245 \tag{29}$$

7.2. *Dual perturbation*

The Smith construction technique applied to the x/x_∞ against time plot yields $T_0 = 7.5$ and $T_1 = 7.5$ min. For the perturbation in inlet concentration, Equation 4 yields $S_{z_1}(\omega) = 0.4 \exp(-\omega^2/0.64)$, then from Equation 3, $\sigma_{z_1}^2 = 0.5672$. Since z_1 and z_2 are mutually independent, the combined spectrum obtained is

$$S_{u+v}(\omega) = S_u(\omega) + S_v(\omega) = 2.7963 \exp(-\omega^2/0.64) + 0.8111/(1 + \omega^2) \tag{30}$$

where $u \equiv \alpha z_1$ and $v \equiv \beta z_2$. Since Equation 15 yields $\hat{\sigma}_1 = 1.8845$ and $\hat{\sigma}_2 = 2.4875$, substitution into Equation 14 leads to $K = 0.4886$ and, in consequence, the output variance is

$$\sigma_x^2 = 1.3352 \int_0^\infty \exp(-\omega^2/0.64)/(1 + 56.25\,\omega^2)\, d\omega + 0.3873 \int_0^\infty d\omega/[(1 + \omega^2)(1 + 56.25\,\omega^2)] = 0.3153 \tag{31}$$

from Equation 1 upon appropriate integration [22, 23].

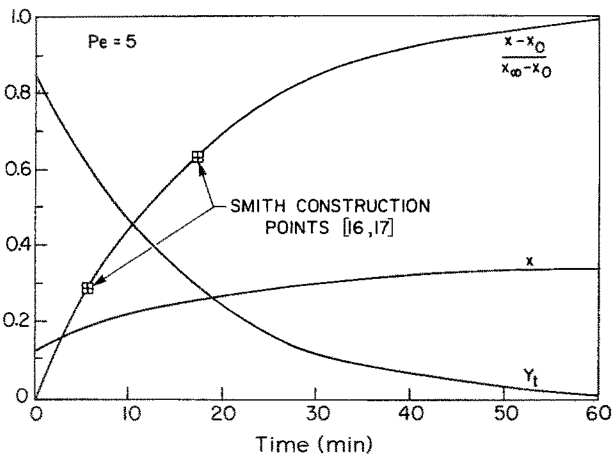

Fig. 2. Step perturbation response via the axial dispersion model [Y_t denotes the multiplier of the $\Delta\Gamma_i$ factor in Equaton 13 of [21]; $x_\infty = 0.3466$].

8. Comparison with electrolyzers possessing deterministic models

The stochastic behaviour of a CSTER with operating parameters given in Table 1 can be predicted in a straightforward manner by the equations of Section 6. Since $\tau = Q/V = 20\,\text{min.}$, the outlet concentration variance is computed as $\sigma_x^2 = 0.007076$ in the single perturbation case, and $\sigma_x^2 = 0.1268$ in the dual perturbation case.

If the PFER model is applied, $\gamma = 0.8221\,\text{min}^{-1}$, $\tau = 20\,\text{min}$ and Equation 22 yields $\sigma_x^2 = 0.282$ in the single perturbation case, and $\sigma_x^2 = 0.774$ in the dual perturbation case. The equivalent gains must be calculated separately in this case since the linear-sum approach via Equation 30 does not apply; the computations yield $K_1 = -1.1682$ and $K_2 = 0.3970$.

Finally, the axial dispersion model requires the computation of Y_t at different times, followed by the computation of x via Equation 23. The analysis of the response shown in Fig. 2 for an axial Peclet number of 5, yields $a = 0.3494$, $b = 0.6506$, $T_0 = -0.192$ and $T_1 = 17.34\,\text{min}$. Since $T_0 \ll T_1$, Equation 26 yields $\sigma_x^2 = 0.0743$ in the single perturbation case and $\sigma_x^2 = 0.568$ in the dual perturbation case. In computing K_1 and K_2 the entrance boundary condition consisting of a local mass balance was replaced by the stipulated step perturbation in the inlet electrolyte concentration, in order to avoid mathematical encumbrances whose treatment under deterministic conditions has been shown elsewhere [21, 24].

Table 2 contains numerical values of the standard deviation of the exit electrolyte concentration, a measure of its stochastic behaviour, and the filtering characteristics (i.e., the reduction of exit concentration fluctuation about its mean) of the electrolyzer types considered. The results indicate that the CSTER is the relatively strongest filter of input randomness, due to its perfect-mixing nature. Conversely, the PFER is the relatively weakest filter due to the complete absence of mixing and the distributive nature of the current perturbation along the electrodes.

The electrolyzer with transient response shown in Fig. 1 is a somewhat weaker filter than the CSTER, the extent of which is determined by its transient response: if the stipulated transient response showed a larger discrepancy with respect to the CSTER transient response, the filtering characteristics would also differ more markedly. The electrolyzer with axial dispersion model predicts a filter characteristic between that of a CSTER and PFER, due to incomplete backmixing associated with axial dispersion (Pe = 5 corresponds to a distinct axial dispersion, permitting neither a CSTER (Pe $\longrightarrow$ 0) nor a (Pe $\longrightarrow$ ∞) approximation).

The foregoing analysis also draws attention to the necessity of experimental response testing as a means of verifying the validity of *a priori* model construction. In the numerical illustration, if the electrolyzer were to operate at an exit dimensionless electrolyte concentration with a fluctuation not exceeding ± 0.1 in the case of a single (current) perturbation, the CSTER model would predict acceptable performance. However, both the PFER and axial dispersion model (Pe $\geqslant$ 5) would predict unacceptable performance, whereas the true performance would be borderline acceptable.

9. Final remarks

The approach presented here has two essential limitations: the first one, linearization involved in the equivalent gain principle, is minimal where the perturbation amplitude effect is not strongly nonlinear.

Table 2. The stochastic behaviour of electrolyzers subject to identical random perturbations in the numerical illustration

Electrolyzer	*Standard deviation of the dimensionless exit concentration*	
	Single perturbation (Current)	*Dual perturbation (Current and inlet concentration)*
Arbitrary, with transient response in Table 2	0.1060	0.5615
CSTER	0.0841	0.3561
PFER	0.5310	0.8798
Axial dispersion Pe = 5	0.2726	0.7537

Standard deviation of dimensionless current: 0.9708
Standard deviation of dimensionless inlet concentration: 0.7531
Standard deviation of combined dimensionless current/inlet concentration: 1.2287

In the case of typical electrolyzers the error of linearization is negligible if the input perturbation amplitudes remain within the stipulated boundaries. The second limitation, the assumption of a Gaussian probablity distribution for the input perturbations is not restrictive, since the Gaussian descripton of many real-life random processes is quite accurate, especially over long observation periods. However, integration in Equation 6 with non-Gaussian density functions can be done numerically if P(z) is known in general, and Equation 6 can be solved analytically in the case of the gamma distribution to yield

$$K = \left(\frac{k\beta^{m+1}}{\sigma_z^2}\right)\left(\frac{\Gamma(\alpha + m + 1)}{\Gamma(\alpha)}\right) \qquad (32)$$

if the dimensionless input parameter has the $(0, \infty)$ domain, the form of the nonlinearity is kz^m; $m > 0$, and α and β are the distribution parameters. In the case of a Weibull distribution with parameters α and β,

$$K = \frac{k}{\alpha^{(m+1)/\beta}}\Gamma\left(\frac{\beta + m + 1}{\beta}\right) \qquad (33)$$

for the same dimensionless input parameter and nonlinearity. The technique has, therefore, wide applicability and its full scope in the analysis of electrochemical reactors should be further explored.

Acknowledgements

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

References

[1] V. V. Solodovnikov, 'Introduction to the Statistical Dynamics of Automatic Control Systems', Dover, New York (1960).

[2] V. S. Pugachev, 'Teoriya Sluchainikh Funkciy' (Random Function Theory) Fizmatgiz, Moscow (1960).

[3] A. A. Pervozvanskii, 'Random Processes in Nonlinear control Systems', Academic Press, New York (1965).

[4] J. H. Laning Jr. and R. H. Battin, 'Random Processes In Automatic Control', McGraw Hill, New York (1956).

[5] H. W. Smith, 'Approximate Analysis of Randomly Excited Nonlinear Controls', MIT. Press, Cambridge, Mass. (1966).

[6] D. Graham and D. McRuer, 'Analysis of Nonlinear Control Systems', Dover, New York (1961).

[7] J. C. West, 'Analytical Techniques for Non-Linear Control Systems', Van Nostrand, Princeton, NJ (1960).

[8] T. Z. Fahidy, *J. Appl. Electrochem.* **17** (1987) 57.

[9] *Idem, ibid.* **17** (1987) 841.

[10] *Idem, Symp. Series, Inst. Chem. Engrs.* (UK) **112** (1989) 119.

[11] *Idem, J. Appl. Electrochem.* The Effect of Random Perturbations On The Performance of Tank Electrolyzers, in press.

[12] J.-C. Gille, M. J. Pélegrin and P. Decaulne, 'Feedback Control Systems', McGraw Hill, NY (1959).

[13] K. H. Lee and T. Z. Fahidy, *Instrum. Control Syst.* **40** (1967) 141.

[14] Y. Sawaragi, N. Sugai and Y. Sunahara, 'Statistical Studies of Nonlinear Control Systems', Nippon Printing and Publishing Co., Osaka, Japan (1962).

[15] J. G. Ziegler and N. B. Nichols, *Trans. ASME* **64** (1942) 759.

[16] C. L. Smith, 'Digital Computer Process Control', Intext Scranton PA (1972).

[17] C. A. Smith and A. B. Corripio, 'Principles and Practice of Automatic Process Control', John Wiley and Sons, NY (1985).

[18] G. H. Cohen and G. A. Coon, *Trans. ASME* **75** (1953) 827.

[19] T. W. Weber, 'An Introduction to Process Dynamics and Control', John Wiley and Sons, NY (1973).

[20] T. Z. Fahidy, 'Principles of Electrochemical Reactor Analysis', Elsevier Amsterdam (1985).

[21] R. W. Yeo and T. Z. Fahidy, *Electrochim. Acta* **31** (1986) 1397.

[22] M. Klerer and F. Grossman, 'A New Table of Indefinite Integrals', Dover, New York (1971).

[23] I. S. Gradshtein and I. M. Ryzhik, 'Table of Integrals, Series and Products', 2nd edition, Academic Press, New York (1980).

[24] R. W. Yeo and T. Z. Fahidy, *Electrochim. Acta* **32** (1987) 277.