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# *Stability of an electrolytic alloy deposition process*

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The stability of electrolytic brass deposition in a continuous flow stirred tank electrolyser is studied via Liapunov functions based on an empirical model of the deposition process.

**Nomenclature**

| | |
|---|---|
| $A$, $B$ | Quantities defined by Equation 8 |
| $C_1$ | Concentration of copper: $C_1^*$, steady state; $C_{1i}$, inlet concentration. |
| $C_2$ | Concentration of zinc: $C_2^*$, steady state; $C_{2i}$, inlet concentration |
| $F$ | Faraday's constant |
| $f_{CN}$ | Free cyanide content |
| $g(x, t)$ | Perturbation vector |
| $i$ | Cathode current density |
| $I_j$ | Current carried by the j-th component (j = 1, copper; j = 2, zinc) |
| $m_1$, $m_2$ | Maximum magnitude of $x_1$ and $x_2$ |
| $m_t$ | Mass of brass deposited on the cathode |
| $M$ | Malkin bound for the partial derivatives of the Liapunov function |
| $M_1$ | Molar mass of copper |
| $M_2$ | Molar mass of zinc |
| $P$ | Symmetric positive definite matrix |
| $q$ | Inlet flow rate of electrolyte |
| $R$ | Relative amount of copper in the bath (%) |
| $t$ | Time |
| $T$ | Reactor temperature |
| $V_r$ | Reactor volume |
| $W_1$, $W_2$, $W_3$ | Positive definite functions (Malkin's theory) |
| $x$ | State vector |
| $x_1$ | Dimensionless copper concentration |
| $x_2$ | Dimensionless zinc concentration |
| $y$ | Relative amount of copper in the brass deposit |
| $z$ | Valency |
| $\gamma^2$ | Liapunov parameter |
| $\varepsilon$ | Bound for the state vector |
| $\eta_1$, $\eta_2$ | Malkin bounds |
| $\lambda_j$ | Time-decay parameter |
| $\mu_1$, $\mu_2$ | Liapunov parameters (non-autonomous system) |
| $\psi$ | Time-decaying perturbation function (vector) |
| $\theta$ | Dimensionless time |

## 1. Introduction

The stability of a CSTER (continuous flow stirred tank electrochemical reactor) with a single electrode reaction at each electrode has previously been treated [1, 2] in terms of Liapunov functions; the approach is purely algebraic and obviates the necessity of solving interlocked nonlinear differential and algebraic equations in order to establish the stability region of a dynamic system. It was shown via the specific case of electrolytic copper deposition that the stability region corresponds essentially to an electrolyte concentration–temperature domain where electrolyte density and conductance can be numerically related to these variables by appropriate statistical regressions. This

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basic finding is independent of the form of perturbation, be it a sudden change in the interior of the reactor or a bounded disturbance in an exterior variable, e.g. the imposed current.

In exploring the scope of Liapunov analysis, the stability behaviour of a CSTER system where two alloying species are simultaneously discharged at a cathode, was recently investigated [3]. The electrolytic production of brass was chosen as a test case due to its familiarity and industrial importance as well as the challenges encountered in correlating pertinent process parameters and variables by a moderately complex mathematical model. The purpose of this paper is to summarize the major findings of the study and to indicate certain practical benefits which may be derived from the approach.

## 2. Summary of the Liapunov method

We consider first the free dynamic system (a system without external forcing):

$$\frac{\mathrm{d}\boldsymbol{x}}{\mathrm{d}t} = \boldsymbol{f}(\boldsymbol{x}, t) \tag{1}$$

with steady state at $\boldsymbol{x} = 0$. If a scalar function $V(\boldsymbol{x}, t)$ with properties

$$V(\boldsymbol{x}, t) > 0; \qquad \boldsymbol{x} \neq 0; \qquad t \geqslant 0 \tag{2a}$$

$$V(\boldsymbol{0}, t) = 0; \qquad t \geqslant 0 \tag{2b}$$

$$\frac{\mathrm{d}V}{\mathrm{d}t}(\boldsymbol{x}, t) = \frac{\partial V}{\partial t} + \frac{\mathrm{d}\boldsymbol{x}}{\mathrm{d}t} \cdot (\text{grad } V(\boldsymbol{x}, t)) < 0; \qquad \boldsymbol{x} \neq 0 \tag{2c}$$

within a certain region $\boldsymbol{x} \in \Omega$ can be found, then any perturbation in this system occurring within region $\Omega$ will let the system return eventually to its original steady state; in other words, the system is asymptotically stable within $\Omega$, and $V(\boldsymbol{x}, t)$ is a Liapunov function. Rigorous treatment and proofs of associated theorems are given by numerous authors (e.g. [4–7]). The simplest algebraic expression for a Liapunov function is the quadratic form $V(\boldsymbol{x}, t) = \boldsymbol{x}^{\mathrm{T}}\boldsymbol{P}(t)\boldsymbol{x}$ where $\boldsymbol{P}$ is a positive definite symmetric matrix; for autonomous *nonlinear* systems the Liapunov function $V(\boldsymbol{x}) = \boldsymbol{f}^{\mathrm{T}}\boldsymbol{P}\boldsymbol{f}$ introduced by Krasovskii [8] has particularly been noted for its relative simplicity. For time-varying perturbations, Berger [9] introduced the Liapunov function

$$V(\boldsymbol{x}, t) = \boldsymbol{x}'\boldsymbol{Q}\boldsymbol{x} + \int_t^\infty \boldsymbol{\psi}'(\theta)\boldsymbol{S}\boldsymbol{\psi}(\theta)\,\mathrm{d}\theta \tag{3}$$

based on the approach of Mangasarian [10], where $\boldsymbol{Q}$ and $\boldsymbol{S}$ are positive definite symmetric matrices and $\boldsymbol{\psi}(t)$ is the set of time-varying perturbations. In the case of persistent perturbations (including external disturbances), stability may be interpreted in terms of Malkin's theorem [11] in the following manner. The dynamic system

$$\frac{\mathrm{d}\boldsymbol{x}}{\mathrm{d}t} = \boldsymbol{f}(\boldsymbol{x}, t) + \boldsymbol{g}(\boldsymbol{x}, t) \tag{4}$$

is stable within a certain region, i.e. $\|\boldsymbol{x}(t)\| < \varepsilon$ if the set of conditions below is satisfied.

(i) The free dynamic subsystem $\mathrm{d}\boldsymbol{x}/\mathrm{d}t = \boldsymbol{f}(\boldsymbol{x}, t)$ is asymptotically stable within a specific region, and $V(\boldsymbol{x}, t)$ is its Liapunov function.

(ii) There exist three positive definite functions, $W_1(\boldsymbol{x})$, $W_2(\boldsymbol{x})$ and $W_3(\boldsymbol{x})$, such that

$$W_1(\boldsymbol{x}) < V(\boldsymbol{x}, t) < W_2(\boldsymbol{x})$$

and

$$\frac{\mathrm{d}V}{\mathrm{d}t} \leqslant -W_3(\boldsymbol{x})$$

(iii) The partial derivatives ($\partial V/\partial x_j$; $j = 1 \ldots n$) of $V(\boldsymbol{x}, t)$ are bounded by a positive scalar $M$.

(iv) For any bounded scalar $\varepsilon > 0$, $\|\boldsymbol{x}(0)\| < \eta_1(\varepsilon)$; $\eta_1 > 0$ and $\|\boldsymbol{g}(\boldsymbol{x}, t)\| < \eta_2(\varepsilon)$; $\eta_2 > 0$

An elegant proof of Malkin's theorem was given in [4]. It is to be emphasized that Liapunov functions are not unique and, more importantly, it is entirely sufficient to find one Liapunov function only to prove stability. However, different Liapunov functions may predict different stability regions and 'maximization' of the stability region implies a systematic search for an 'optimal' Liapunov function. This otherwise intriguing aspect of the theory is well beyond the scope of the current paper.

## 3. Modelling of the electrolytic brass process

Brass, the first and one of the most widely used alloy-plating processes to be produced by electrodeposition, is plated from cyanide solutions at low current densities (about $0.5\,\mathrm{A\,dm^{-2}}$) for decorative purposes. While several texts discuss brass-plating process technology in detail (e.g. [12–16]) there have been relatively few in-depth investigations of the inter-relationship between various process parameters and deposit quality [17–23] which would allow a full description of the plating process via a mathematical model. An effort to combine all pertinent experimental data into one comprehensive model [3] has not been successful and it appears that specific process models developed on the basis of individual literature references offer the best opportunity to proceed: in this paper the model based essentially on Field's data [18] is employed for the analysis of stability. The most important process parameters are the copper to zinc ratio in the electrolyte, current density, free cyanide content, ammonia content, temperature, pH and the total metal content, although not every parameter can be related in an acceptable quantitative manner to deposit quality. Similarly, colour and current efficiency are difficult to account for numerically, these factors placing a certain constraint on the applicability of mathematical models. The data obtained by Field were correlated via the multidimensional regression

$$y = b_0 + b_{11}T + b_{21}R + b_{31}f_{CN} + b_{32}f_{CN}^2 + b_{33}f_{CN}^3 + b_{41}i + b_{43}i^3 + b_{51}if_{CN} \qquad (5)$$

with parameter values given in Table 1 and statistical information in Table 2; the ratio of the sum of squares of the regression to the total sum of squares is reasonably close to the ideal value of unity (i.e. when all data variations are accounted for by the model). Although the data are based on steady-state experimental conditions, it may be assumed with reasonable certainty that the relative copper content of the deposit is independent of the duration of electrolysis, since according to Ferguson and Sturdevant [20] the relative copper content varied by only 4% in the first 50 h of an 88-h electrolysis. Thus, Equation 5 may be used as a component of a dynamic mass balance equation

*Table 1. Multivariable regression on data obtained by Field [18]: parameter values*

| *Regression parameter* | *Value* | *Standard error* |
|---|---|---|
| $b_0$ | 26.3766 | 13.8529 |
| $b_{11}$ | 0.2578 | 0.1698 |
| $b_{21}$ | 1.4952 | 0.1199 |
| $b_{31}$ | −6.4202 | 2.5151 |
| $b_{32}$ | 0.4342 | 0.1878 |
| $b_{33}$ | 0.0077 | 0.0035 |
| $b_{41}$ | −21.0938 | 3.5180 |
| $b_{43}$ | 0.9309 | 0.3109 |
| $b_{51}$ | 0.4139 | 0.1126 |

*Table 2. Multivariable regression on data obtained by Field [18]: statistical information*

| *Source* | *Degrees of freedom* | *Sum of squares* | *Mean square* | A/B |
|---|---|---|---|---|
| Model | 8 | 10580.199 (*A*) | 1322.63 | 0.8713 |
| Error | 37 | 1562.728 | 42.24 | |
| Total | 45 | 12142.927 (*B*) | | |

for describing a continuous brass deposition process in a well-stirred flow reactor consisting of a single-compartment cell with a pair of parallel plate (steel) electrodes. The operating conditions are summarized in Table 3.

The mass balance equation in unsteady state may be formally written as

$$V_r \frac{dC_j}{dt} = q(C_{j,i} - C_j) - \frac{I_j}{Z_j F} - G; \qquad j = 1, 2 \tag{6}$$

where the function $G$ represents the overall effect of the plating parameters. In terms of the dimensionless concentration perturbation variables, $x_j = (C_j - C_j^*)/C_{j,i}; j = 1, 2$ and dimensionless time $\theta = qt/V_r$, the dynamic state equations

$$\frac{dx_1}{d\theta} = -x_1 - A = f_1(x_1, x_2) \tag{7a}$$

$$\frac{dx_2}{d\theta} = -x_2 + B = f_2(x_1, x_2) \tag{7b}$$

are obtained, where

$$A = \frac{m_t}{qC_{1,i}tM_0}(y - y^*) \tag{8a}$$

*Table 3. Operating variables and conditions of the brass deposition process*

*Reactor*
Dimensions: $0.7 \times 0.7 \times 0.7\,\text{m}$
Active volume: $V_r = 0.343\,\text{m}^3$

*Electrodes*
Active area: $A_e = 0.4624\,\text{m}^2$
Thickness: $d = 0.002\,\text{m}$
Separation distance: $s = 0.68\,\text{m}$

*Operating conditions at steady state*
Inflow rate: $q = 10^{-6}\,\text{m}^3\,\text{s}^{-1}$
Current density: $i = 0.5\,\text{A}\,\text{dm}^{-2}$
Inlet copper concentration: $C_{1,i} = 0.4865\,\text{kg}\,\text{m}^{-3}$
Inlet zinc concentration $C_{2,i} = 0.3532\,\text{kg}\,\text{m}^{-3}$
Effluent copper concentration: $C_1 = 0.3463\,\text{kg}\,\text{m}^{-3}$
Effluent zinc concentration: $C_2 = 0.3059\,\text{kg}\,\text{m}^{-3}$
Free cyanide content: $f_{CN} = 9.0\,\text{kg}\,\text{m}^{-3}$
Percentage copper in deposit: $y = 74.2\%$

*Dominant ionic species in electrolyte*: $Cu(CN)_3^{2-}$ and $Zn(CN)_4^{2-}$

and

$$B = \frac{m_t}{qC_{2,i}tM_2}(y - y^*) \tag{8b}$$

and the perturbation variable $(y - y^*)$ is related to the state variables $x_1$ and $x_2$ by

$$y - y^* = 1.494581\left(\frac{30.91x_1 + 22.0}{30.91x_1 + 23.09x_2 + 42.0} - 0.5238\right)$$

It is instructive to note that the brass deposition model is represented in a 'modular' form by Equation 8, where the functional form of the $(y - y^*)$ term is determined by the specific deposition model used. (In [3] five independent models for electrolytic brass deposition are presented.) The variables $x_1$ and $x_2$ are the *state variables* of the process.

## 4. Liapunov analysis of the brass deposition process

### 4.1. *Perturbation in the state variables*

For the sake of illustrating Liapunov's stability method, two 'candidate' functions will be considered. The first one employs a positive definite matrix in its quadratic form, and the second is based on Krasovskii's theorem ([6]; see also Appendix 1). In the first instance

$$V(x_1; x_2) = x_1^2 + \gamma^2 x_2^2 \tag{9}$$

where $\gamma^2$ is an a priori indeterminate scalar. Although $V(\boldsymbol{x})$ is positive–definite for all values of $x_1$ and $x_2$, and it is zero when $x_1 = x_2 = 0$, the negative definiteness of its time derivative

$$\frac{1}{2}\frac{dV}{d\theta} = -x_1^2 - \gamma^2 x_2^2 - Ax_1 + \gamma^2 Bx_2 \tag{10}$$

cannot be ascertained by inspection. A systematic evaluation of the derivative [3] indicates that its negative definiteness is guaranteed if $0.001 < \gamma^2 < 10$. The numerical value of $\gamma^2$ is immaterial, it only alters the shape of the $V(\boldsymbol{x})$ contours enclosing the regression domain. (Stability analysis outside the regression domain is indeterminate, since a mathematical model of the brass deposition process is constrained to the validity range of the regression.) Consequently, Equation 9 shows that no perturbation in $x_1$ and/or $x_2$ originating inside the regression domain will cause instability; the perturbed process will return to its set steady state.

The analysis based on Krasovskii's theorem yields the quadratic form

$$\begin{aligned} V(x) &= (f_1 f_2)\begin{pmatrix} 1 & 0 \\ 0 & \gamma^2 \end{pmatrix}\begin{pmatrix} f_1 \\ f_2 \end{pmatrix} \\ &= x_1^2 + \gamma^2 x_2^2 + A^2 + \gamma^2 B^2 - 2Ax_1 - 2\gamma^2 Bx_2 \end{aligned} \tag{11}$$

which has to be positive–definite. In order for its time-derivative to be negative–definite, the inequalities

$$1 + \frac{\partial A}{\partial x_1} > 0$$

$$4\gamma^2\left(1 + \frac{\partial A}{\partial x_1}\right)\left(1 - \frac{\partial B}{\partial x_2}\right) - \left(\frac{\partial A}{\partial x_2} - \gamma^2\frac{\partial B}{\partial x_1}\right)^2 > 0 \tag{12}$$

have to be satisfied (see Appendix). In terms of numerical values pertaining to the model, the

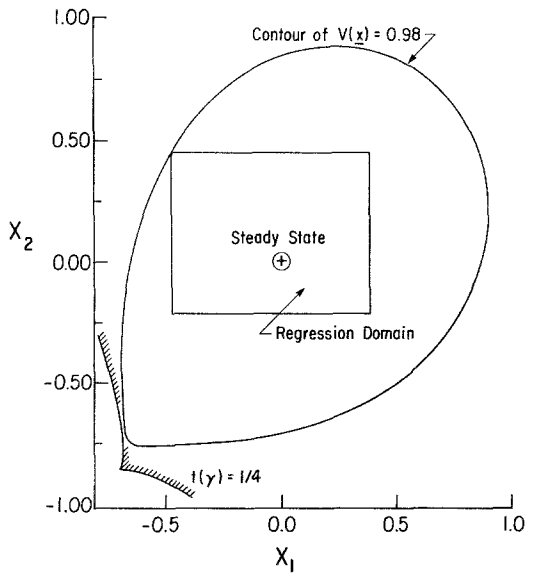


Fig. 1. Illustration of Krasovskii's method ($x_1$ = dimensionless copper concentration; $x_2$ = dimensionless zinc concentration in electrolyte).

conditions of asymptotic stability are

$$D > -0.0557 \tag{13a}$$

and

$$4\gamma^2(1 + 17.94D)(1 + 17.94E) - (13.04E + 24.02\gamma^2 D)^2 > 0 \tag{13b}$$

where

$$D = \frac{23.09x_2 + 20.0}{(30.91x_1 + 23.09x_2 + 42.0)^2}$$

and

$$E = \frac{30.91x_1 + 22.0}{(30.91x_1 + 23.09x_2 + 42.0)^2}$$

Since both $D$ and $E$ are positive within the regression domain, the first inequality is immediately satisfied. The second inequality, rewritten as

$$f(\gamma) = \gamma^2 \frac{(1 + 17.94D)(1 + 17.94E)}{(13.04E + 24.02\gamma^2 D)^2} > \frac{1}{4} \tag{14}$$

can be satisfied within the regression domain, where $0.0068 < D < 0.0340$ and $0.0044 < E < 0.0167$, only for a certain set of values of $\gamma^2$. The choice of $\gamma^2 = 1$ provides a Liapunov contour that encloses the regression domain without traversing the boundary defined by $f(\gamma) = 1/4$, as shown in Fig. 1. Hence, Krasovskii's method also indicates asymptotic stability within the regression region.

### 4.2. *Perturbations due to time-decaying external and parameter forcing*

A typical case of external forcing is shown by variations in inlet composition, represented by the dimensionless variables

$$\psi_j \equiv \frac{C_{j,i} - C^*_{j,i}}{C^*_{j,i}}; \qquad j = 1, 2 \tag{15}$$

If such variations are time-decaying in the exponential sense, i.e.

$$|\psi_j(t)| < \psi_j^0 \, \varepsilon^{-\lambda_j t}; \qquad j = 1, 2 \tag{16}$$

where $\psi_j^0$ is the magnitude of $\psi_j$ at zero time, the analysis of stability follows closely Mangasarian's approach [10] modified by Berger [9]. An appropriate Liapunov function

$$V(\boldsymbol{x}, \theta) = x_1^2 + \gamma^2 x_2^2 + \int_0^\infty [2\mu_1 \psi_1^2(\theta) + 2\mu_2 \psi_2^2(\theta)] \, \mathrm{d}\theta \tag{17}$$

with its time derivative

$$\frac{1}{2}\frac{\mathrm{d}V}{\mathrm{d}\theta} = -x_1^2 - \gamma^2 x_2^2 - \mu_1 \psi_1^2 - \mu_2 \psi_1^2 - A x_1 + \gamma^2 B x_2 + \gamma^2 \psi_2 x_2 \tag{18}$$

carries a priori indeterminate positive parameters $\mu_1$ and $\mu_2$ in addition to the familiar $\gamma^2$ parameter. If $\mu_1$ and $\mu_2$ are chosen to be sufficiently large, $\mathrm{d}V/\mathrm{d}t$ will always be negative, and at large times when $\psi_j \to 0$, the conditions of 4.1. are regained. Since the numerical values of $\mu_1$and $\mu_2$ are immaterial, asymptotic stability within the regression domain follows directly in the case of external forcing of this kind, including simultaneous initial perturbations in the electrolytic bath concentrations. In the case of parameter perturbations the state equations may be rewritten as

$$\frac{\mathrm{d}x_1}{\mathrm{d}\theta} = -x_1 - A(\theta) \tag{19a}$$

and

$$\frac{\mathrm{d}x_2}{\mathrm{d}\theta} = -x_2 + B(\theta) \tag{19b}$$

where $A(\theta)$ and $B(\theta)$ are explicit functions of time incorporating all parameter-forcing effects. Equation 9 is a valid Liapunov function with time derivative

$$\frac{1}{2}\frac{\mathrm{d}V}{\mathrm{d}\theta} = -x_1^2 - \gamma^2 x_2^2 + \gamma^2 B(\theta) x_2 - A(\theta) x_1 \tag{20}$$

and asymptotic stability can again be ascertained provided that the forcing functions do not exceed the range limitations of the parameters in the regression model.

4.3. *Persistent perturbations in external forcing*

When external forcing is persistent but bounded, stability in the Malkin sense can only be considered, as shown in Section 2; asymptotic stability loses its sense since a continuously perturbed system cannot reach a steady set of state variables. A typical illustration of this kind of forcing is bounded perturbations in the electrolytic current (or potential drop between oppositely charged electrodes). For the free dynamic subsystem excluding the current-carrying vector term $g(\boldsymbol{x}, t)$ in Equation 4

$$\frac{\mathrm{d}x_1}{\mathrm{d}\theta} = -x_1 \tag{21a}$$

and

$$\frac{\mathrm{d}x_2}{\mathrm{d}\theta} = -x_2 \tag{21b}$$

a valid Liapunov function is given once again by Equation 9 with negative–definite time derivative

$$\frac{1}{2}\frac{\mathrm{d}V}{\mathrm{d}\theta} = -x_1^2 - \gamma^2 x_2^2$$

Further, $W_1(\boldsymbol{x}) = 0$; $W_2(\boldsymbol{x}) = m_1^2 + \gamma^2 m_2^2$; $|x_1| \leqslant m_1$; $|x_2| \leqslant m_2$; $W_3(x) = x_1^2 + \gamma^2 x_2^2$ are permissible (as well as logical) choices. The bound of the $\partial V/\partial x_j$ partial derivatives may be taken as $M = 2(m_1^2 + \gamma^4 m_2^2)^{1/2}$, and the bound $\eta_1$ is completely arbitrary as long as $\eta_1$ is positive. The bound for the perturbation vector $\boldsymbol{g}(\boldsymbol{x}, t)$ must satisfy the condition

$$\eta_2 > ([-A(\theta)]^2 + B^2(\theta))^{1/2}$$

which implies again an arbitrarily large positive scalar. Finally, an obvious choice for the state-variable bound is $\varepsilon = (m_1^2 + m_2^2)^{1/2}$; hence, all conditions of Malkin's theorem being satisfied, Malkin stability has been proven.

## 5. Comparison of the Liapunov stability analysis with electrolyser response to perturbations

In order to illustrate the validity of the foregoing stability analysis, transient responses of the brass deposition process obtained via digital computer simulation are compared with the former. Fig. 2 portrays the return to steady state of the process perturbed by five sets of sudden change in electrolyte composition within the regression domain where the indicated stable behaviour is predicted by Equations 9 and 10. Stability in the case of time-decaying perturbations is illustrated in Fig. 3, and Fig. 4 depicts a typical transient response to a sinusoidal perturbation in current of the form

$$i = \bar{\imath} + \Delta i \sin(\omega\theta) \tag{22}$$

In Table 4 representative values of the Malkin stability parameters are assembled. These parameters were obtained from corresponding transient responses similar to those given in Fig. 4.

## 6. Conclusions

It has been demonstrated in this paper that stability analysis based on appropriately chosen Liapunov functions is a fast and relatively straightforward means of studying the stability of simultaneous metal deposition via electrolysis: there is no need to solve the governing state equations for each set of process perturbations. However, the success of the approach depends strongly

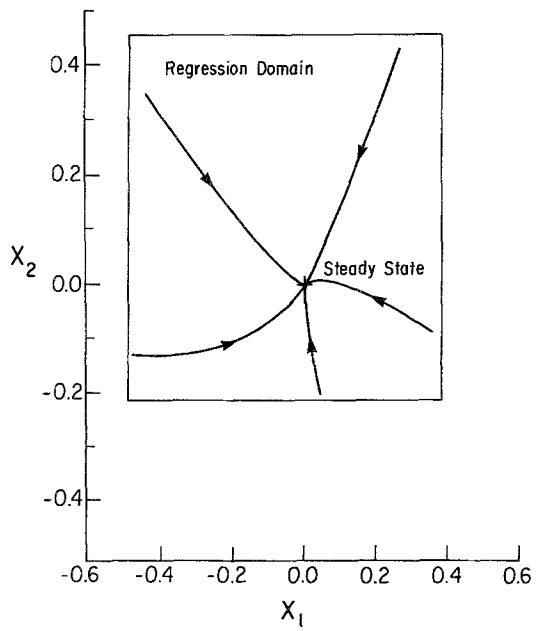


Fig. 2. Transient response to five sets of sudden perturbation in the electrolyte composition (coordinates defined in caption of Fig. 1).

*Table 4. Malkin stability parameters from transient responses to periodic forcing in current (Equation 22)*

| $\omega$, $h^{-1}$ | $x_1$ | | $x_2$ | | $m_1$ | $m_2$ | M | $\eta_2(\varepsilon)$ | $\varepsilon$ |
|---|---|---|---|---|---|---|---|---|---|
| | *Min* | *Max* | *Min* | *Max* | | | | | |
| 1.0 | −0.13 | 0.39 | −0.14 | 0.17 | 0.39 | 0.17 | 0.94 | 10.79 | 0.42 |
| 0.5 | −0.16 | 0.44 | −0.22 | 0.21 | 0.44 | 0.22 | 1.13 | 10.83 | 0.49 |
| 0.1 | −0.40 | 0.69 | −0.64 | 0.52 | 0.69 | 0.64 | 2.47 | 11.01 | 0.94 |

$\bar{i} = 0.5\,A\,dm^{-2}$; $\Delta i = 0.25\,A\,dm^{-2}$.
$\gamma = 1.232$ (arbitrary choice).

on the availability of electrochemical and physical data and their quantitative dependence on dominant process variables. The present scarcity of such information poses a serious limitation on the scope of this powerful technique and underlines the importance of extending the available data base for electrochemical systems.

The existence of stability, while important for process control considerations, is not a guarantor of acceptable overall performance, since undesirable cathode quality can be temporarily produced during (large) transient response periods. In the specific case of brass deposition, for example, deposit colour and composition may be adversely affected, at least over short periods of time, and the suppression of large perturbations would be an overriding control objective regardless of inherent long-term stability. While an integral part of rational process design, stability analysis does not obviate other considerations and it has to be employed in a proper perspective.

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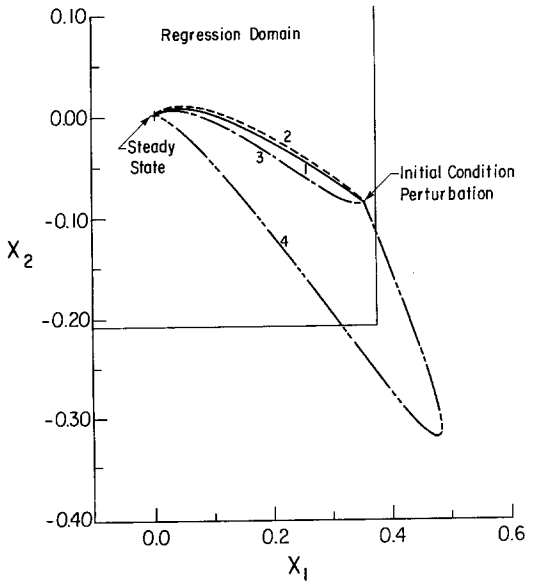


Fig. 3. Transient response to various perturbations (coordinates defined in caption of Fig. 1).

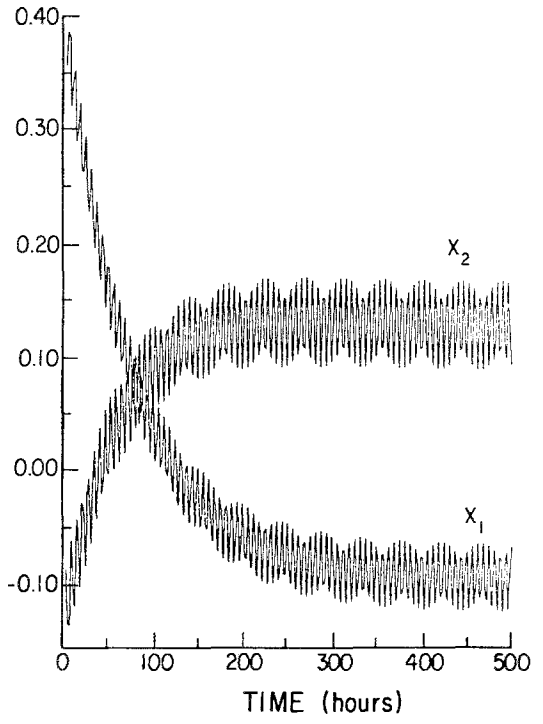


Fig. 4. Transient response to sinusoidal forcing in current density $\bar{i} = 0.5\,\mathrm{A\,dm^{-2}}$; $\Delta i = 0.25\,\mathrm{A\,dm^{-2}}$; $\omega = 1\,\mathrm{h^{-1}}$ (coordinates defined in caption of Fig. 1).

## Appendix

*Construction of a Liapunov function by Krasovskii's method [6]*

For the system represented by the state vector differential equation

$$\frac{\mathrm{d}\boldsymbol{x}}{\mathrm{d}t} = f(\boldsymbol{x}); \qquad \boldsymbol{f(0)} = \boldsymbol{0} \tag{A.1}$$

the quadratic form

$$V(\boldsymbol{x}) = \boldsymbol{f}^{\mathrm{T}}\boldsymbol{P}\boldsymbol{f} \tag{A.2}$$

is a Liapunov function; the positive definite matrix $\boldsymbol{P}$ is a priori indeterminate. Differentiation of Equation A.2 yields

$$\frac{\mathrm{d}V}{\mathrm{d}t} = \boldsymbol{f}^{\mathrm{T}}(\boldsymbol{P}\boldsymbol{J} + \boldsymbol{J}^{\mathrm{T}}\boldsymbol{P})\boldsymbol{f} = -\boldsymbol{f}^{\mathrm{T}}\boldsymbol{Q}\boldsymbol{f} \tag{A.3}$$

where $J$ is the Jacobian matrix of the system, i.e. $J = \{\partial f_i/\partial x_j\}_n$ and $\mathrm{d}\boldsymbol{f}/\mathrm{d}t = \boldsymbol{J}\boldsymbol{f}$. Hence, for proving asymptotic stability, the matrix $\boldsymbol{Q} = -(\boldsymbol{P}\boldsymbol{J} + \boldsymbol{J}^{\mathrm{T}}\boldsymbol{P})$ must be positive-definite. Let $\boldsymbol{Q}$ be a $2 \times 2$ square matrix, as in the case of interest here, with diagonal elements $q_{11}$, $q_{22}$. Then, for positive definiteness the Sylvester inequalities [24]

$$q_{11} > 0 \tag{A.4}$$

$$\det \boldsymbol{Q} = q_{11}q_{22} - q_{12}q_{21} > 0 \tag{A.5}$$

must be satisfied. The shortcoming of this simple and elegant method is its conservativeness in predicting the size of the region where the system is stable, especially if the identity matrix is chosen for $\boldsymbol{P}$ as a simplification. If, for example, $f_1 = x_2$ and $f_2 = -2x_1 - 3x_2$, the resulting $q_{11} = 0$ violates Equation A.4 and the method fails although the system is asymptotically stable everywhere with real negative eigenvalues of $-1$ and $-2$.

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