



Towards information processing from nonlinear physical chemistry: A synthetic electrochemical cognitive system

Saman Sadeghi^a, Michael Thompson^{b,*}

^a Crump Institute for Molecular Imaging, UCLA, 570 Westwood Plaza, Building 114, Los Angeles, CA 90095, USA

^b Bioanalytical Chemistry, Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario M5S 3H6, Canada

ARTICLE INFO

Article history:

Received 5 February 2010

Accepted 2 August 2010

Keywords:

Electrochemical dynamics
Perturbation response
Information processing
Complex systems
Emergent patterns
Spatiotemporal attractors

ABSTRACT

It is evident that complex animate materials, which operate far from equilibrium, exhibit sensory responses to the environment through emergent patterns. Formation of such patterns is often the underlying mechanism of an active response to environmental changes and can be interpreted as a result of the distributed parallel information processing taking place within the material. Such emergent patterns are not limited to biological entities; indeed there is a wide range of complex nonlinear dissipative systems which exhibit interesting emergent patterns within a range of parameters. As one example, the present paper describes the detection of emergent phenomena associated with surface electrochemical processes that allow the system to respond to input information through evolving patterns in space and time. Associative mapping of this sort offers the opportunity to devise an electrochemical cognitive system (ECS), where pattern formation can be looked at as a macroscopic phenomenon resulting from the extensive distributive computing that occurs at the microscopic level.

© 2010 Elsevier Ireland Ltd. All rights reserved.

1. Introduction

1.1. Computers, Patterns and Brain Functioning

Information processing has come to be synonymous with computer architecture and software design, where, in terms of the latter, the “mimicking” of biological neural mechanisms to date has been restricted to parallel processing and neural network programs. Accordingly, the operation of current computers on the basic hardware level is fundamentally primitive when compared to brain functioning. It is clear, then, that a material system is required which based on its internal dynamics can better resemble nature. Before embarking on a possibility for this exercise we briefly examine some key ingredients of brain operation.

We do not know how the mind works, nor can we say with much certainty whether the source of our higher consciousness is intrinsic to the material construct of our brain. What we can say is that the brain, like any complex dynamic configuration generally operates in far from equilibrium conditions and pattern formation is a generality and the norm in such systems. These patterns arise from the activity of a network of neuronal elements that permit cognitive phenomena. Thus, pattern formation can be interpreted

as the result of a distributed parallel computing taking place *inside* a material.

Our brain is capable of modeling the world around us and recognizing and responding to slight changes to any one of the many models it has stored (Barlow, 1990). At any given moment the brain is dealing with a large number of variables provided to it by the body's sensory systems and is capable of simultaneously processing this time-varying multivariable information and forming an appropriate command in response to the changing environment. The brain can be described as an information processing system working in conjunction with the body to recognize and respond to the environment. The representation of information is provided to the brain in the form of neural activity received from the body's sensory arsenal. The senses play the role of transducers, translating the information as efficiently as is possible, to a language with which the processing system can work. This information is then recognized as belonging to certain categories with memories and links associated with each. There may perhaps be extended layers of such categories and complex links forming between them. The information and memories called up from certain recognized states may then evoke specific neuronal signals which demand a physiological response. This expression of the brain's interpretation is carried out by the body which can be thought of as output transducers enabling action in the physical world. Understanding this process leads to several parallels with the biologically inspired electrochemical information processing system introduced in the present work.

* Corresponding author. Tel.: +1 4169783575; fax: +1 4169788775.

E-mail addresses: samsadeghi@mednet.ucla.edu (S. Sadeghi), mikethom@chem.utoronto.ca (M. Thompson).

1.2. The Role of Patterns in the Brain

We can look at the brain as a dynamical system capable of forming patterns (Haken, 1996). The state of such a dynamical system at any given time can be defined with a set of variables which can fully describe the system. We will be adopting this definition of a dynamical system since it can also be applied to other complex systems that are composed of many variables, such as chemical reactions described through a set of interacting species. As mentioned above, the state can be represented in vector form $x = (\xi_1, \xi_2, \dots, \xi_n)$ with each ξ_i describing one of the variables necessary for a full description of the system. Now the internal evolution dynamics of the system, which can occur through interaction of its elements as well as with outside perturbations, can change certain components ξ_i , thereby changing the state vector x as function of time. We can describe this temporal change of any single variable as a function of itself and other variables in the system at time t described by the vector x_t , and a set of external perturbations that can affect the system as described by the vector λ_t . We can write this as follows:

$$\frac{d\xi_i}{dt} = F_i(x_t, \lambda_t) \quad (1.1)$$

In this way the time evolution of the state will be given by set of functions F each describing the change in a single variable which can be written as follows:

$$\frac{dx}{dt} = F(x_t, \lambda_t) \quad (1.2)$$

If we describe the human brain in terms of the state of neurons, we can readily see that in order to analytically quantify its temporal evolution we would have to solve about 10^{11} equations, one for each ξ_i representing a neuron which itself has about 10^4 interconnections that define its state (Amit, 1989). Therefore, the analytic power of brain may be viewed as a system which is indeed capable of continuously solving these 10^{11} equations each with 10^4 variables. The result of this massive operation taking place in the brain is a set of emergent patterns with many defining features that are distinct to data provided to it by the body's sensory organs.

It is safe to say that all significant cognitive events in the brain take place on the larger scale resulting from the cooperative activity of elements within the network (Haken, 2002, 2004, 2006). Individual neurons only compute by being appropriately connected to large numbers of similar units and elementary cognitive phenomena such as retrieval from memory and recognition, are represented by patterns of activity of the network of these units. Pattern formation in this way, can be looked at as a means of information processing. In the field of computer science, this idea of emergent collective computational capability has been studied through neural network programs (Hopfield, 1982), which to the present time, have been confined to simulation on computers with serial processing architectures.

1.3. Intelligent Signal Processing

One of the pillars of human cognitive abilities is the power of decision making. In general this process requires analysis and recognition of situations encountered in the past, from incomplete information provided in the present. In fact, there is often a finite set of decisions or actions that are plausible for the situation and our cognitive ability may in this way be reduced to problem classification and selection of appropriate action. This is very much analogous to pattern recognition, whereby we are confronted with either a very complex, distorted or incomplete set of information or a classification decision is needed. In all cases, either due to the sheer complexity of the data or simple incomplete presentation, we are faced or must resort to making a decision from a subset of infor-

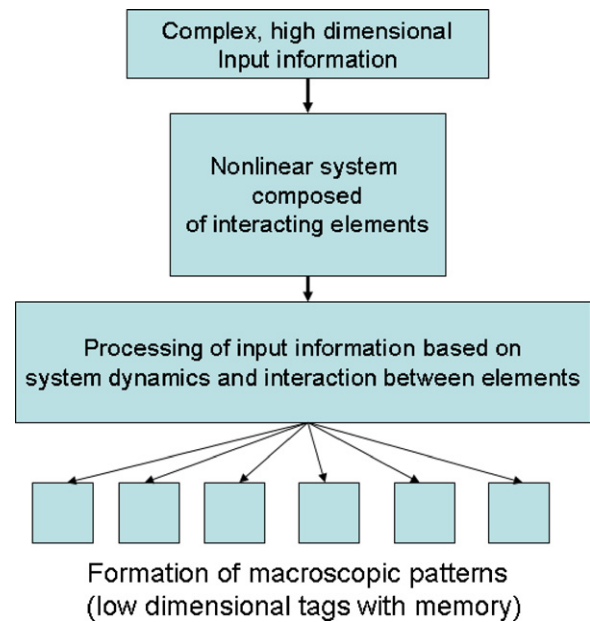


Fig. 1. Basis for information processing based on emergent patterns.

mation. We can see here that the problem of feature extraction, where the essential bits of information necessary for classification and recognition are recognized, is inexorably intertwined with information processing and cognitive abilities.

An abstract model of how a pattern forming system might perform computation in a manner similar and inspired by the brain is illustrated in Fig. 1. There are a number features in the scheme proposed here which form the basis of a biologically inspired information processing system. Such a system has the capability to compress a set of similar input information to a discrete number of recognition states. The mapping of data in this manner allows both for recognition from incomplete sets of information and a recall memory associated with the data.

The power of a system which can carry out the proposed scheme will be related to its ability to process a large amount of information, in the same way as the brain deals with data from sensory transducers, in a fast and reliable manner. For this purpose we have to look to a physical system, whose defining properties or unique spatiotemporally distributed states can serve as the recognition flags and memory for particular sets of information. The idea of data storage using localized structures of physical system (Coulet et al., 2004a) and emergent computation through spatially extended systems such as cellular automata has been reported in the literature (Crutchfield, 1994; Crutchfield and Mitchell, 1995; Delgado and Sole, 1997). Such a physical system may be regarded as an adaptive filter whose properties are changed by the input signals which are provided to it (Kohonen, 1989). In this way, a particular set of input signals would act as keys which would evoke recognition responses and stored information associated with the key events. Nonlinear dynamical systems possess the capability to exhibit these properties and will be investigated as the medium to create such a system in this paper.

2. Complex Physical Systems and Cognition

2.1. Connection Between Patterns and Complex Systems

We have suggested that there is a link between pattern formation and distributed computation and this plays a pivotal role as a means of information recognition in the brain. It is now important

to note that pattern formation is in fact an inherent phenomenon in nonlinear systems that operate away from equilibrium. Biological systems are full of interesting and functional patterns that arise as the result of their interrelated dynamics (Nicolis, 1987; Koch and Meinhardt, 1994). With the ground breaking paper on morphogenesis (Turing, 1952), Turing, through an elegant set of activator, inhibitor reactions and diffusion equations created a blueprint of systems which can exhibit a departure from homogenous states and form stable spatial patterns.

In short, pattern formation, which we have proposed as a basis of cognition, has a strong connection to nonlinear phenomena found in complex physical systems. There has been extended theoretical research in this field during the past few decades and several models have been proposed. These are either based on outside-equilibrium thermodynamics which point to the onset of dissipative structures (Nicolis and Prigogine, 1977; Maseko, 2003) or kinetic models which make use of simplifications and compromises in order to describe and predict the behavior of the nonlinear dynamic system (Kiss, 1988; Cross and Hohenberg, 1993; De Wit, 1999; Ertl, 2002; Burke and Knobloch, 2006).

Systems that can be described by differential equations can exhibit changes from simple to complex behavior in response to changes in their control parameters. For example, chaotic and periodic motion can be seen even in the case of a periodically forced and damped pendulum which has only a few degrees of freedom (Gollub and Langer, 1999). Furthermore, sequences of increasingly complex spatiotemporal patterns can be observed if we look to dynamical systems with many degrees of freedom described through partial differential equations. Such equations can model the interrelated evolution of variables which describe the system. Mathematical models of these systems often have multiple steady state solutions for a set of initial conditions, and have the capability to jump from one solution to the next or choose a preferred steady state based on changes in the parameters which have an influence on the system. The steady states are often described as attractors in phase space, which is a multidimensional theoretical space that is spanned by the dynamical variables of the system. In this way, every unique point in the phase space describes a particular set of values or a state, which portrays the system in an instant of time. Thus we can visualize the dynamics of the system in terms of trajectories which track its evolution from one state to the next. An attractor is then a steady state that can range from a homogenous arrangement of the system to temporal or spatial patterns ranging from simple one frequency oscillations to more complex arrangements. It is the utilization and application of these preferred attractor patterns in response to specific parameters that is the focus of this work. Fig. 4 illustrates a phase space representation of patterns, where each spatially distributed state vector as shown in 3A is represented by a dot in the subset of the phase space shown in 3B. The path taken is the temporal evolution of the states. Two simple examples of oscillatory behavior (the closed loop) and relaxation to a node state via different paths are shown in this state space subset.

2.2. Associative Memory

Associative memory is closely linked with pattern formation and recognition (Vanderwolf, 1998), and can be defined as a system which stores a set of patterns, $x^{(p)}$, $p=1, 2, \dots, k$ in its internal state, and produces the copy of a particular set $x^{(r)} = (\xi_1^{(r)}, \xi_2^{(r)}, \dots, \xi_n^{(r)})$, $r \in \{1, 2, \dots, k\}$ to the output when presented with the any signal from the set of $x^{(i)} = (\xi_1, \xi_2, \dots, \xi_n)$ in which a specified subset of values ξ_i matches with the corresponding subset of the $\xi_i^{(r)}$.

However for a system like the one considered here, the reply is stored in form of attractors $x_t^{(r)} = (\omega_1^{(r)}, \omega_2^{(r)}, \dots, \omega_m^{(r)})$ for m being the number of tags associated with $x^{(r)}$, in which every element of the reduced dimensional, time dependent signal $x_t^{(r)}$ is a tag of $x^{(r)}$ associated with a particular aspect of $x^{(r)}$. In this way we can ensure invariant representation of equivalent stimuli such as geometrical transformation of input information I giving rise to the same tags $x_t^{(r)}$.

This also ensures the optimized and efficient utilization of the available memory states, whereby only the most significant aspects of $x^{(r)}$ are stored and recalled through associative memory. This kind memory and recall association is also a commonly utilized method in biological systems. For example we can recognize the face of a friend or a general emotion such as anger through a few distinct features. These features are tags which are constant in pictures which may have been taken under different conditions or in case of emotions from different people.

The tags are in effect the patterns generated by the electrochemical system studied here, which are simpler and more invariant than the original occurrence of information provided to the system. They can be looked at as discrete eigenfeatures of the input information, and may be understood as the result of discrimination by a system which automatically categorizes all input data with similar prominent features, thus distinguishing aspects of input information. Classification of new occurrences with a set composed of existing tags from other $x_t^{(r)}$, can be looked at as making an educated guess. This is analogous to making a link or being unable to distinguish between stimuli which share a common set of features and are provided under constraints of limited or imperfect cues. Furthermore, linking relations between input information can be established by looking at the number shared tags between various data. The input information $x^{(i)}$ can be in the form of a multidimensional array I , such as a two-dimensional array σ^2 for an image or a three dimensional array σ^3 with an added dimension of time.

We can understand the mapping dynamics through a changing internal state S of the system, which when presented with a set of input information I , produces a time varying output signal $x_t^{(r)}$ which is a function of the internal state and I at time t . To formalize this let us consider two mapping functions: f for the internal state where,

$$f : S^{(t+1)} = f(S^{(t)}, I^{(t)}) \quad (2.1)$$

and g for the output, where,

$$g : x_t^{(r)} = g(S^{(t)}, I^{(t)}) \quad (2.2)$$

Here the internal state of the system S is complex and depends on all variables which are required to fully describe the electrochemical system. The state $x_t^{(r)}$ on the other hand is the set of observable tags which have associations attached to them and can be significantly simpler than I and S . The processing power of the system is essentially encompassed in the state S and the mapping functions g and f .

The input information may or may not have time dependency. If the input information, I , is time independent, then the tags associated with I may be spread in time and emerging with some time delay, all describing a particular aspect of I . In the case of a time dependent $I^{(t)}$, given $I(t=0)$ the full output time series $\{x_t^{(r)}\}_{t=0 \rightarrow t}$ may be generated and in this way the future behavior of $I(t)$ predicted from system response when the system is presented with a single element $I(0)$. Furthermore, time delay in an electrochemical system is analog and continuous as supposed to finite time delay in digital circuits.

The input information may have a particular context C associated with it, whereby the information presented to the system is composed of $(C, I(t))$ where C can be presented by the DC offset of the input signal in the electrochemical system, and I the AC and spatial component of the perturbation. Different C factors are equivalent to the experiments performed under different control parameters, where the system may evolve differently giving rise to distinguishable patterns $\{x_t^{(r)}\}_{t=0 \rightarrow t}$, and thus discriminating between input information based on the context in which the information was presented to the system.

When a sufficient superset of $\{x^{(r)}\}$ tags are associated with input information superset $\{I\}$, and the system is presented with new information I_1 , which is inherently different in elements but sufficiently similar to sets I_2 and I_3 , it may invoke an output $x^{(r)}$ that is a subset of combined sets $x^{(2)} + x^{(3)}$. The system can be thought of as synthesizing a new kind of information based on innovative association. Such innovative recognition has been suggested in the form of unintended attractors that have been observed in simulations of recurrent attractor neural networks (Yoon et al., 1995).

2.3. Electrochemical Implementation

One possible mechanism to achieve the form of computation proposed here is pattern formation that can be instigated during the electrodisolution of metals. Experimental evidence for the existence of a wide variety of temporal patterns in such systems was observed as early as 1978 (Frank, 1978; Lev et al., 1988), and there have been more recent studies on spatial patterns (Ertl, 1991; Hudson and Bassett, 1991). This has been complimented with more recent theoretical work that has established a basis for formation of temporal and spatial patterns during electrodisolution of metals, based on coupled ODEs and PDEs describing elements of the system such as concentration and double layer potential (Flatgen and Krischer, 1995).

The occurrence of spatiotemporal patterns during electrochemical reactions is related to the interplay between reaction rates given by the Butler–Volmer equation and the mass action diffusion given by Fick's laws which bring a time dependency into the picture; this is further complicated by the structure of the double layer and its time dependence which gives rise to changing migration currents. Furthermore, surface reactions, geometry of the cell and electrode as well as external controls must be taken into consideration.

Pattern forming electrochemical systems display a region of negative differential resistance in their current–potential characteristic (Koper, 1998), which in addition to the natural kinetic driving force of any increase of potential, manifests an activator–inhibitor system. In activator–inhibitor type electrochemical systems, the potential takes on the role of activator while the inhibitor is a chemical quantity such as the concentration of the electroactive species or the coverage of the electrode. Spatial inhomogeneities in activator and inhibitor can induce migration and diffusion fluxes respectively, which in turn lead to the occurrence of electrochemical pattern formation. The main difference from a reaction diffusion system, like that of Turing's, is that in contrast to diffusion, migration represents a long range spatial coupling (Mazouz and Krischer, 2000). Furthermore, the transport mechanism in electrochemical systems is mostly influenced by migration rather than diffusion (Mazouz et al., 1997). In this way, local perturbations in the double layer potential are mediated through the electric field in the liquid phase (Levart and Schuhman, 1970). Thus, spatial inhomogeneities in the double layer potential are felt not only by nearest neighbors but by a whole range of neighboring sites.

The representative equations for the electrochemical system examined here are related to reaction diffusion type dynamics since they can be described by a local function and a spatial coupling

term. Furthermore, global coupling is routinely present in electrochemical experiments and could play a stabilizing or destabilizing role in the dynamics, acting as an activator as well as an inhibitor depending on the electrochemical reaction under consideration (Krischer et al., 2000). The strength of this global coupling may be readily varied since it is introduced by an external control circuit (Kiss et al., 1999).

A theoretical understanding for electrochemical kinetics of metal electrode dissolution can be considered through a model based on coupled differential equations that take time variance of defining parameters into account. There are a number of conditions in electrochemical systems that depend on coupled parameters governed by nonlinear dynamical laws. When a metal electrode is immersed in liquid electrolyte, ions from the metal surface will dissolve until a junction potential is created due to the charge imbalance. This potential, E_0^0 , under standard conditions is specific to each metal dissolution process and is related to the free energy of cell reaction by considering that during the completion of the cell reaction, the transfer of charge nF is affected. Under equilibrium conditions this potential is influenced by metal ions activity a_M in the electrolyte as can be derived from basic thermodynamic principles and is given by the Nernst equation,

$$E_0 = E_0^0 + \frac{R}{n} \frac{T}{F} \ln \left(\frac{a_{M^{n+}}}{a_M} \right) \quad (2.3)$$

We can remove this system away from equilibrium to promote the formation of dissipative patterns through the application of an overpotential $\Delta\phi$. The resulting kinetics, describing the nonlinear effect of polarization on the current density due to charge transfer polarization are described by the Butler–Volmer equation. However, when the concentration of reacting species at the electrode surface is lower than that of electrolyte, the flux of ions becomes the rate controlling factor. Mass transfer may be due to either diffusion, which depends on concentration gradients or migration which is the movement of charged species under an electric field. Convection which is due to fluid motion is not discussed here since the electrolyte solution in our experiments was not stirred. As discussed, mass transfer plays an important role in providing local and long range coupling and communication in pattern formation during electrochemical dissolution.

When the electrode processes take place according to diffusion kinetics the steady state current passing through the working electrode is given by Fick's first law:

$$J = -D \left. \frac{\partial c}{\partial x} \right|_{x \rightarrow 0} \quad (2.4)$$

where J is the diffusion flux [$\text{mol m}^{-2} \text{s}^{-1}$], c concentration [mol m^{-3}] and D diffusion coefficient [$\text{m}^2 \text{s}^{-1}$] with temperature dependence of,

$$D = D_0 e^{-(E_A/RT)} \quad (2.5)$$

for E_A representing the activation energy for diffusion [J (mol)^{-1}]. $\left. \frac{\partial c}{\partial x} \right|_{x \rightarrow 0}$ is the concentration gradient in the immediate vicinity of the electrode.

The time variance of concentration plays a role in pattern formation (see Fig. 3) and we can relate the time differential to concentration gradient through Fick's second law, which can be derived from the first law of diffusion and mass balance:

$$\frac{\partial c}{\partial t} = -\frac{\partial}{\partial x} J = D \frac{\partial^2 c}{\partial x^2} \quad (2.6)$$

or $D \nabla^2 c$ in three dimensions, considering that the diffusion coefficient does not change with coordinates. In case of steady state, Fick's second law gives a linear concentration profile near the working electrode. It is therefore necessary for complex tempo-

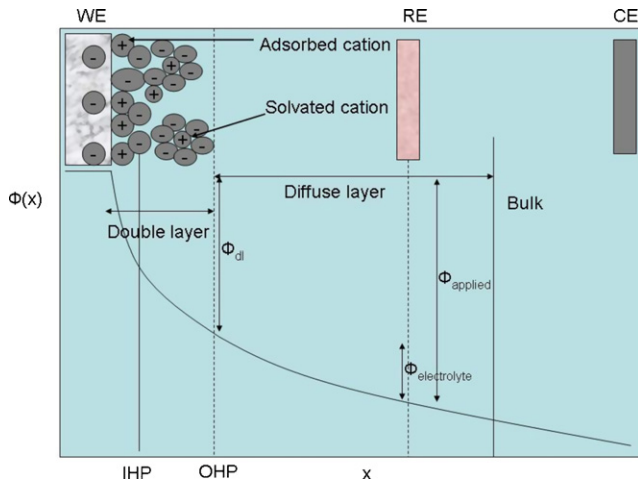


Fig. 2. The electrical double layer. Depending on concentration, the electrolyte side of the double layer can extend up to 10 nm and can be thought of being made of various layers. The most common model defines two layers. The inner Helmholtz layer is given by the distance of the plane passing the centre of the specifically adsorbed hydrated ions to the metal surface. The outer Helmholtz layer is defined by the distance of the solvated ions to the working electrode which are held in their structure by electrostatic forces.

ral behavior that concentration should exhibit a minimum second order variation with respect to spatial coordinates.

Similarly, migration current flux is the result of potential gradient described as follows:

$$J_m = -\frac{zFDc}{RT} \frac{d\phi}{dx} \quad (2.7)$$

Further to these coupled differential equations describing the relation of concentration, potential and current, a phase boundary is formed when a metal electrode is brought into contact with the liquid electrolyte. The subsequent rearrangement of electric charges to achieve equilibrium in each phase due to charge transfer and adsorption of ions among other factors gives rise to a structured and distributed electric potential difference in the boundary layer known as the double layer. As illustrated in Fig. 2, at a given potential hydrated ions will accumulate in front of the working electrode and will balance an equal excess charge in the metal. The thickness of the charge layer in the metal is less than 1 angstrom and can safely be assumed to be of zero thickness (Fig. 2 is not to scale). A diffuse layer connects the outer plane to the bulk solution. The thickness of the diffuse layer depends on the concentration of the solution.

We can solve for the structure of the double layer by considering,

$$\frac{d^2\phi}{dx^2} = -\frac{\rho(x)}{\epsilon\epsilon_0} \quad (2.8)$$

for $\rho(x)$ representing the charge density and $\phi(x)$ potential obeying the Poisson's equation. From this relation, a differential equation for the inner potential can be derived which can be linearized to give,

$$\frac{d^2\phi}{dx^2} = \kappa^2\phi(x) \quad (2.9)$$

for κ representing the Debye inverse length.

The dynamics and coupling of the afore-mentioned controlling parameters can illustrate the theoretical basis of pattern formation ranging from oscillatory to spatial and temporal patterns spanning from chaos to orderly regimes and transitions in the phase dynamics (Krischer et al., 1991; Jaeger et al., 2002).

The stability of the system defined in this way, through a set of linear differential equations, requires an evaluation of the change

in small perturbations of both the double layer potential and concentration at the stationary points through the Jacobian matrix:

$$\begin{pmatrix} \frac{d\delta\phi_{dl}}{dt} \\ \frac{d\delta c}{dt} \end{pmatrix} = J_{\phi_{dl}^s, c^s} \begin{pmatrix} \delta\phi_{dl} \\ \delta c \end{pmatrix} \quad (2.10)$$

If the eigenvalues of J are both negative, the fixed point is stable; the steady state is otherwise unstable. The stability of the system can also be studied with an evaluation of the largest Lyapunov exponents which is calculated for the results presented here. Through control and perturbation of parameters which influence the electrochemical system, it is possible to cause a sign shift in the eigenvalues of J and therefore direct the evolution of the dynamics and bifurcations in the system.

The evolution of the system can be pictured in a phase space whose coordinates are concentration and double layer potential. Fig. 3A shows the null cline curves ($d/dt=0$) of the ϕ_{dl} and concentration. It is simple to see that the steady state of the system is where the two curves intersect, since at such a point both dc/dt and $d\phi_{dl}/dt$ are zero. Furthermore, the time derivative of each variable, which determines the direction of movement in phase space, changes sign as the corresponding null cline curve is crossed. Since the double layer potential changes much more rapidly than concentration, being off the steady state, the system will move much faster in the horizontal direction to reach the double layer steady state than in the vertical direction. Furthermore, the direction will be dictated depending on which side of the null cline the system resides at a given time. Once on the potential null cline curve, the system will then slowly move toward the concentration null cline. This perturbation off the steady state is illustrated in Fig. 3, where the final relaxation point of the system is the single steady state value.

If however, a situation as in Fig. 3B is considered, then it can be seen that the intersection occurs on the negative slope of the ϕ_{dl} nullcline, where the direction in which ϕ_{dl} changes in this neighborhood points away from the steady state. On the contrary, the change in concentration points toward the steady state. Since the ratio of potential to concentration time scale is small, the dynamics are such that ϕ_{dl} changes much more rapidly than concentration. This promotes an oscillatory behavior, where the system evolves on the potential null cline and jumps from one branch to another without ever reaching the steady state.

Considering the dynamics of the system in the phase plane illustrated in Fig. 3C shows a division of two different basins of attraction. Any system parameters starting or being perturbed to one side of the separatrix, which divides the phase space into different basins, will arrive at a particular attractor. That is to say it will either oscillate or arrive at a steady state.

The spatially homogenous dynamics that we have considered so far have ignored the evolution of other variables which affect the dynamics at the electrode/electrolyte interface. Such variables can include the coverage of the adsorbates on the surface of the electrode, adsorption processes, migration, surface reactions and structural phase transition processes at the electrode surface. These and other extensions and refinements of this described model can be found in the literature (Bertram and Mikhailov, 2001, 2003).

The number of coupled time dependent elements in ECS makes a full analytical model rather impossible to solve without the aid of simplifying assumptions. However, from an experimental perspective, these relations provide the needed ingredients to form a sufficiently complex system capable of producing a range of spatiotemporal patterns. Furthermore, the coupling can be fine-tuned which permits control over the appearance of patterns and transitions between them.

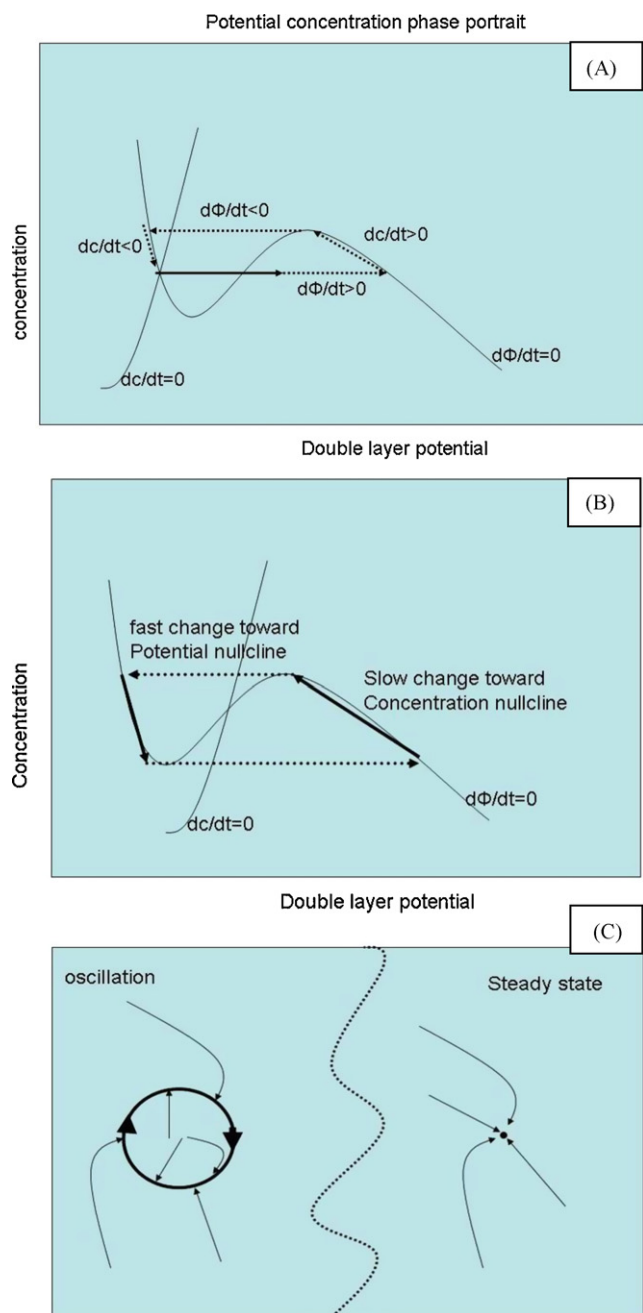


Fig. 3. Panel A is a representation of a perturbation leading to steady state. Solid arrow indicates a perturbation, and the dashed arrows show the path of flow and evolution of the system following a potential perturbation. Panel B is a representation of possible oscillations mechanism in the phase portrait. Panel C is a representation of basins of attraction for the two variable temporal model of the electrochemical system.

These dynamics are complimented by inherent short term history dependence in the dynamics, due to the location of ECS in the phase space at any moment (Fig. 4). Furthermore, longer term history dependence is possible as a result of surface changes on the working electrode and feedback training mechanism can be created whereby, upon recognition of the input of information, perturbations are repeated to strengthen a particular pattern by making use of slow variations in the internal resistance of a ferroelectric layer that can be embedded beneath the working electrode or the use of software weighing factors.

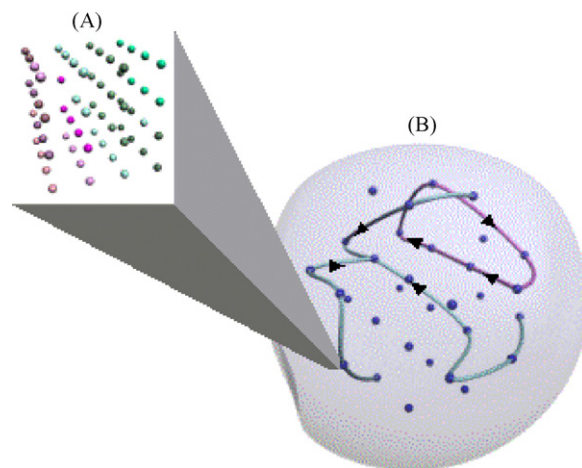


Fig. 4. Multidimensional phase space subset.

2.4. Properties of Pattern Forming Electrochemical Systems

An appraisal of some of the underlying mechanisms in electrochemical processes reveals features that are entirely appropriate and necessary for a complex configuration to behave as a pattern forming system:

- (1) Far from equilibrium conditions and criteria for nonlinearity are evident in the kinetic equations of electrochemistry.
- (2) Instant, long range communication and parallel dynamics are made possible by spatial transport of ions through the classic equations of reaction, diffusion and convection, as well as the migration of charges inside the electrolyte. Temporal patterns which affect the changing of the double layer potential are dependent on coupled differential equation which can be derived from both mass transfer and charge balance (Krischer, 2001; Christoph and Eiswirth, 2002).
- (3) Feedback mechanisms exist, which together with the dynamics of ECS, lead to phase transitions, multiple stability points, sustained oscillations, strange attractors and chaotic behavior.

Accordingly, in tandem measurement and control of ECS, offers the harnessing of the computational capabilities that arise from the underlying nonlinear reaction, diffusion and drift dynamics with long range interconnection that take place between these processes three-dimensionally inside the electrolyte and on the surface. This highly distributed activity leads to the formation of patterns in a reasonable time, which is the analog of the computational mapping of the input information that had affected the processes. In summary, we can formalize the idea of pattern formation as a means to facilitate information recognition by describing recognition as formation of localized phase structure with identifiable features that can effectively categorize and store tags on input information. This is tantamount to a processing power which arises from within the dynamics of the material.

2.5. Localized Phase Structures as Recognition States

An ideal cognitive device, one that can potentially outperform digital computers, will exhibit the ability to classify complex input information in a content addressable way. The recognition of the content and indexing can be performed in a fault tolerant manner based on the dynamics of the system which are sensitive to input parameters. These dynamics would be performing the role of massively parallel computers working to recognize the input data and retrieve their associated memory.

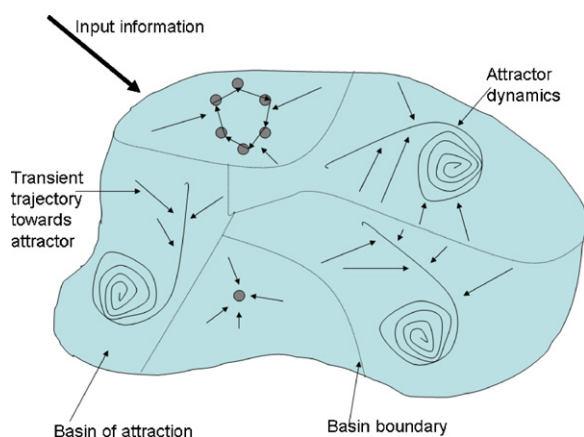


Fig. 5. Cognitive phase space, depicting multiple coexisting attractors.

Emergent pattern formation in nonlinear systems can perform this task of recognition from imperfect data through evolution of their dynamics toward a particular attractor. The attractor is chosen from a set of coexisting attractors which form the phase space of the system. Fig. 5 is an illustration of phase space dynamics where, depending on input perturbation, the system finds itself in one of the many basins of attraction and thus converges to evolve on the specific evolution path of that attractor. The stable solutions of the differential equations proposed in the previous section can represent just such attractors. There have also been attempts to characterize the maximum information that can be stored in a medium by relating the formation of such patterns to generalizations of Shannon's channel capacity (Coullet et al., 2004b).

As the attractor only occupies a portion of the phase space there is an inherent compression of the input information. This compression is the result of the reduced degrees of freedom as the initial stimulus is forced to evolve from a set of N degrees of freedom, forming the information phase space to that of D_i degrees of freedom which defines the information dimension of the attractor (i) towards which the stimulus relaxes. In the case of strange attractors which exhibit a non integer dimension, such as the reported 2.05 dimension of a Lorenz attractor (Grassberger and Procaccia, 1983), a compression factor of $N-D_i/N$ of 32% is afforded. This compression factor ensures a measure of fault tolerance during information processing by the system. A progressive increase in compression accommodates a larger basin of attraction for a particular attractor, allowing stimuli with larger Hamming distances to relax to the same recognition state.

The information dimension of the particular attractor can be thought of as the level of abstraction which allows segmentation of large variety of external world information into a few significant categories. There is an obvious advantage of compressibility and ease of recognition with simpler attractors. Ideal compression systems are for example stable steady state solutions or singular nodes in the phase space, which would have a 0 information dimension, while oscillatory limit cycles would have a dimension of 1. It is clear however, that homogeneous states and attractor patterns have no capacity to store information and that a periodic pattern only contains information about a wave number and the position of one vertex. The information dimension of the attractor can play the role of dynamically retrievable memory which shows up in form of patterns produced by the attractor. The experimental results reported here, point to the existence of multiple coexisting strange attractors in the electrochemical system. These attractors possess positive and negative Lyapunov exponents λ , with $|\lambda_-| > |\lambda_+|$ (Eckmann and Ruelle, 1985). These strange attractors while still squeezing the dimension of input information due to the larger $|\lambda_-|$, have the

capacity to create a specific and nontrivial response based on the emergent pattern of the attractor. Such attractors, in comparison to steady state patterns which perform poorly as memory storage devices, can exhibit associative memory recall functionality.

3. Electrochemical Experimentation

3.1. Experimental Apparatus

The schematic design of the system is illustrated in Fig. 6. The working electrode, reference electrode, electrochemical cell, and parts of the data acquisition system were developed or assembled in our lab. All data acquisition, storage and analysis were performed with National Instrument's Labview and a few optimized signal processing libraries written in c, running on a specifically architected network of computers which were necessary due to the high volume of data and the need for real time analysis.

Information through defined oscillatory voltage perturbations are coded in terms of spatiotemporally varying voltages and provided to the electrochemical system. Input data, such as voice through a microphone and visual scenes through a camera can be coded as perturbation to ECS with resulting currents acquired and analyzed in real time with the aid of networked computers. In this way, the computer algorithms characterize the patterns, effectively translating the emergent patterns to tags that are readily recognizable by the user.

Voltage perturbations are conditioned through re-sampling and scaling and delivered to the working electrode such that alterations are within a reasonable range. A working electrode is designed to pick up the spatiotemporally resolved response of the electrochemical system at any given time as well as to provide perturbations. The working electrode is an array of Ni wires with only the tips exposed to the electrolyte. The electrochemical cell is controlled by a potentio/galvanostat as well as the spatially distributed voltage provided to the working electrode. Additional external control and interaction is imposed by enforcing a constant temperature and electrolyte concentration. Current-to-voltage conversion through a shunt external resistor is used to interface with the data acquisition system. Digital data is analyzed in real time is also automatically time stamped, labeled and stored for future offline analysis.

By adding long term history dependence, the system can also respond to its own reaction, adjusting its behavior based on its present and previous responses. This adjustment can modify the perturbation which the system receives, and may for example take the form of blocking any further perturbation (stubbornness) or increasing the scale of information (attention).

3.2. Electrochemical Cell

The working electrode was designed to be used for spatiotemporally resolved data acquisition. Each element of the working electrode is a nickel insulated wire which was from Goodfellow (Pennsylvania, US). The insulation was composed of polyimide. The nickel itself was 99.0% pure Ni with a conduction diameter of 0.25 mm and outside diameter of 0.28–0.30 mm Fig. 6C. The array was designed to have an exposed face surface for the metal/solution interface to exist. To ensure there was no other contact between the electrodes and the solution the electrodes were surrounded by a cast resistant to high concentration H_2SO_4 electrolyte used in experiments. The epoxy used for casting was obtained from Paisley Epoxies (Toronto, Canada), which had a stated viscosity of ~150 cPs. The viscosity of the epoxy was an extremely important factor since the polymer had to penetrate between the close proximity of the nickel electrodes and seal the 200 μm gaps so that no air bubbles persisted. The epoxy was treated with a low pressure vacuum

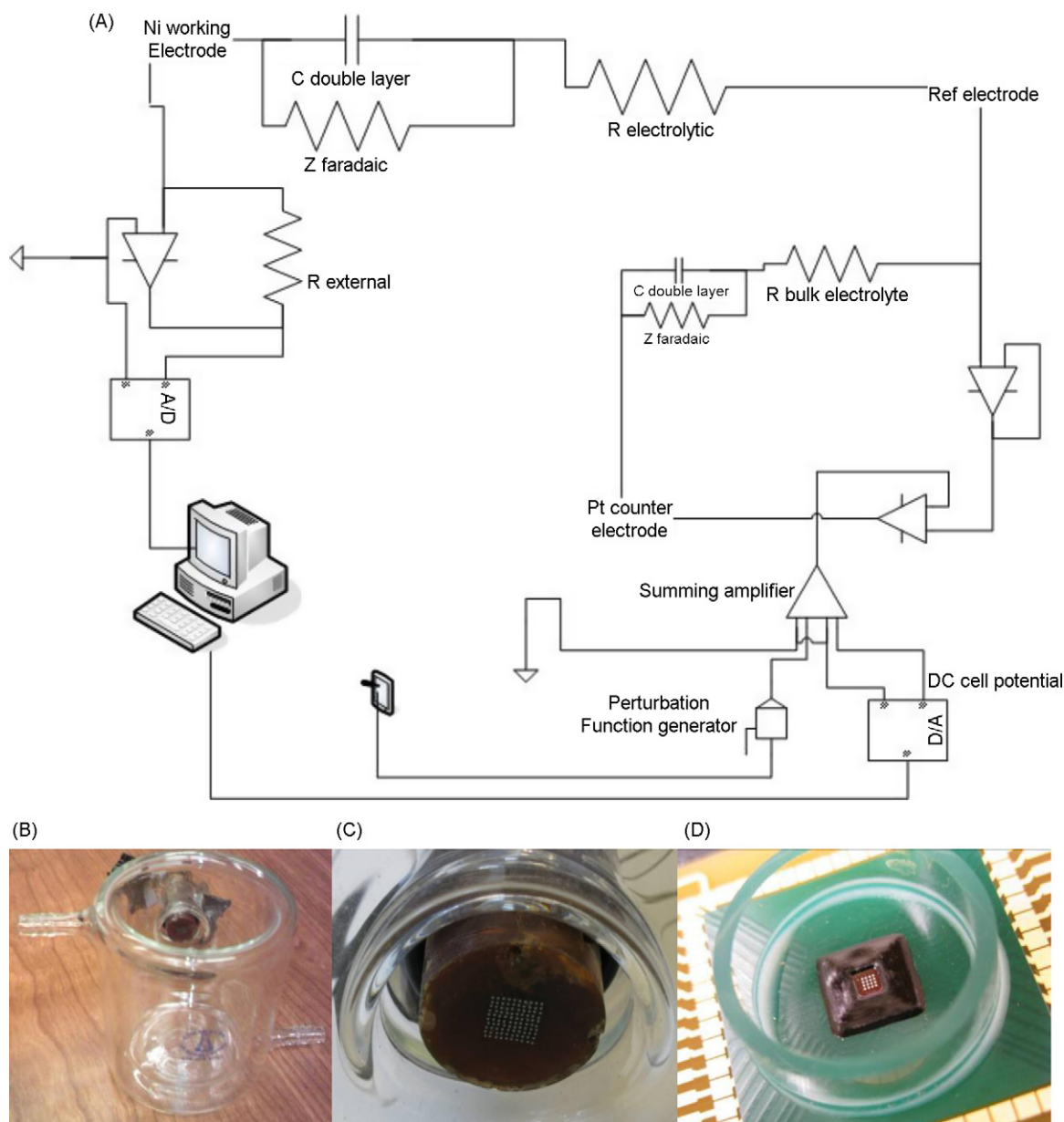


Fig. 6. System layout schematic in panel A shows the introduction of information through the perturbation function generator and their coding into the system along with other control parameters such as potentiostatic control, through the summing amplifier. A simplified electrical model for the electrochemical reaction produces the current signal which is conditioned and digitized from each nickel working electrode. The computer decodes and translates the system output and provides a feedback loop by relaying the system response to effect the subsequent input information. Panel B shows the temperature controlled electrochemical cell and panel C is a close up of the microelectrode array, showing the spatially distributed electrode array. Panel D is a prototype integrated miniaturized system.

to dispose of air bubbles before curing. The epoxy required a 6 h pre-curing time at 60 °C followed by a 14 h curing time at 100 °C in an oven. Fig. 6D shows a miniaturized cell with an integrated electrode array which was developed through a collaboration with the fabrication group at Tyndall National Institute in Ireland. The arrays in this setup were electroplated in a low stress nickel sulphamate bath at 50 °C.

The counter electrode was a platinum mesh of sufficient surface area such that the cathodic reaction would not be limiting. The mesh was connected through a copper wire which was protected by an epoxy layer from direct or capillary contact with electrolyte. The reference electrode was from Radiometer Analytical, with an Hg/Hg₂SO₄ electrode in a saturated K₂SO₄ filling solution (0.658 vs. NHE at 22 °C). The electrode was specifically chosen to avoid chloride contamination in the electrolyte since the role of chloride

ions in attacking passivation films (Scully, 1987) and interference with the nature of temporal instabilities (Sazou and Pagitsas, 1991) is documented in the literature.

3.3. Data Acquisition and Analysis

The data acquisition was performed in three stages of current-to-voltage conversion, voltage amplification and digitization. Once in digital form, the data was analyzed and stored in real time with the use of networked computers.

A 16 bit National Instrument data acquisition board with 100× amplification before digitization was used giving an effective digitization resolution of 3.5 nA. The acquisition of current was achieved by the use of a 1000 Ω precision shunt resistor in the path of the current and measurement of the voltage drop across the resistor. This

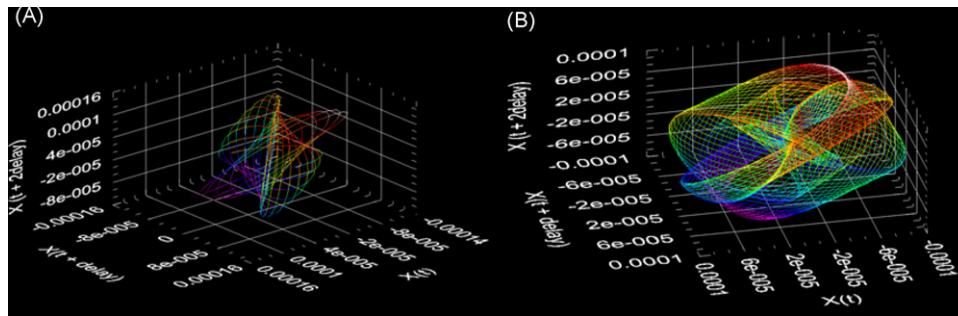


Fig. 7. Time delay plot. Original data from temporal patterns extracted from (A) Nickel wire with exposed area of 0.049 mm², showing 50 ms of data and (B) copper with exposed area of 5 mm², showing 100 ms of data, is displayed together with 10 and 20 ms delays after applying a bandpass filter.

resistor essentially played the same role as that of external circuit resistance which also influences the nature of temporal patterns (Zhai et al., 2004).

The presence of temporal dynamics approaching the kilohertz region, which were significantly faster than other systems such as Belousov-Zhabotinsky reactions with periods in order

of minutes, required particular attention in the instrumentation design to capture these patterns with high resolution (Vanag and Epstein, 2007). Temporal patterns reported here were acquired at 20,000 samples/second or at least 5 times the highest frequency in the signal, well above the Nyquist requirement.

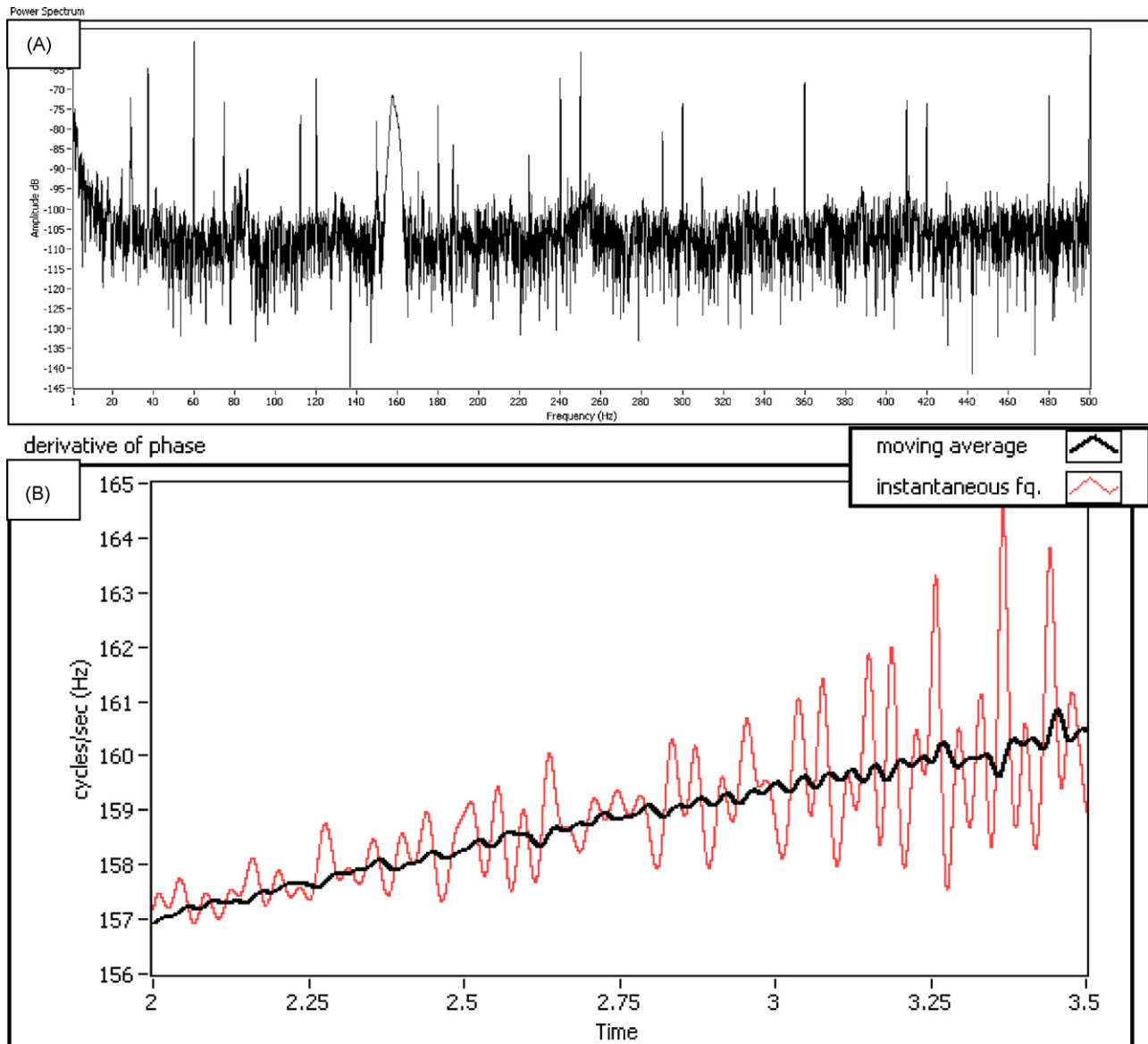


Fig. 8. Panel A is a power spectrum of a 5 s data segment following a 1 s 150 Hz perturbation, showing the stimulated system response in form of activity band spanning approximately 10 Hz. Panel B illustrates the drift in the frequency of the response pattern revealing the nontrivial dynamics of the patterns generated by the system.

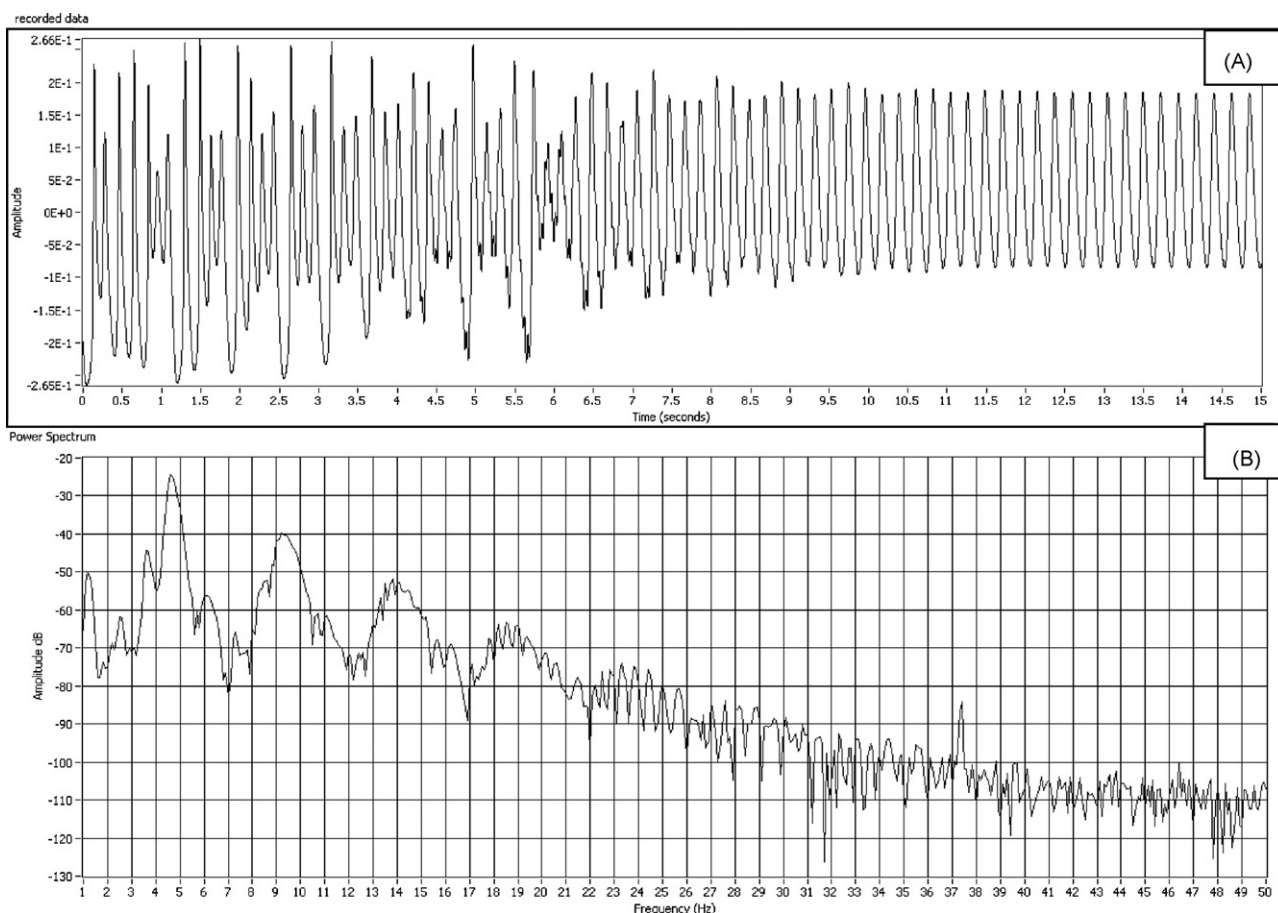


Fig. 9. Panel A shows the raw data which is stimulated by a 23 Hz signal with the onset of 4 s and lasting for 5 s, causing a transformation in the dissolution patterns. Panel B is a power spectrum of current response between 10 and 15 s (after the removal of stimulus) acquired from the nickel wire. The spectrum shows the nontrivial response of the system with several frequencies and their harmonics ranging into 50 Hz region which allows for the characterization of patterns and recall of information stored in the 10 s of milliseconds timeframe.

With the goal to create a real time recognition and information processing unit, special effort was made to implement real time acquisition and analysis methods. A TCP/IP data communication channel was created between networked computers, where the primary computer was mainly in charge of acquisition and control. The signal processing, storage and real time interpretation load was handled by networked computers which could then, through their networked architecture, influence the control parameters based on the results of analysis.

Information was provided to the system in form of voltage perturbations at 20% of the RMS amplitude of the base temporal activity, delivered to the working electrode through an analog output channel on the NI card. Two particular modes of perturbation were investigated. One was in the form of constructed sinusoids of various frequencies and amplitude. After the system reached the region of interest chosen from the polarization curves V_0 , a sinusoidal signal was superimposed onto the applied potential with frequency $2\pi\omega$ and amplitude A so that the applied potential became,

$$V_{app}(t) = V_0 + A \sin(2\pi\omega t) \quad (3.1)$$

The other mode was based on vocal frequencies as recorded from a microphone, digitized by a sound card, conditioned by the software and converted back to analog voltages on the NI card. Provisions were made in the software to allow feedback perturbations based on the real time analysis results from networked computers. Feedback may be used to push the system to a progressively more stable state (Lin et al., 2000), and may be obtained through propo-

tional perturbation of the applied voltage equal to the difference of the total current $I_{tot}(t - \tau)$ and the mean total current $I_{tot,mean}$ (Kiss et al., 2006). The applied potential would then be,

$$V_{app}(t) = V_0 + K(I_{tot}(t - \tau) - I_{tot,mean}) \quad (3.2)$$

where K is the gain and τ is a time delay. In case of multiple electrodes the total current was obtained by summing the individual currents.

4. Results and Discussion

The patterns exhibited by ECS range from oscillatory to chaotic and require signal processing techniques for quantitative feature extraction. The time delay plots in Fig. 7 show examples of unsteady attractors which the temporal patterns can exhibit. As the only acquired variable from ECS is current and there are other variables such as concentration and double layer potential which also influence the dynamics of the system, time delay plots are employed to extract more data from the single acquired element by adding delayed data sets of the original (Fraser and Swinney, 1986).

Other techniques used for analysis of data from ECS included frequency power spectrums, to extract distinct frequencies and their harmonics as well as time-frequency analysis to examine the phase and energy dynamics of various frequency components. Of course one can envision a setup, where this task of feature extraction is also performed by a cascade of electrochemical systems to a point where the outputs can be directly connected simpler functioning mechanism such as a series of amplifiers that respond to

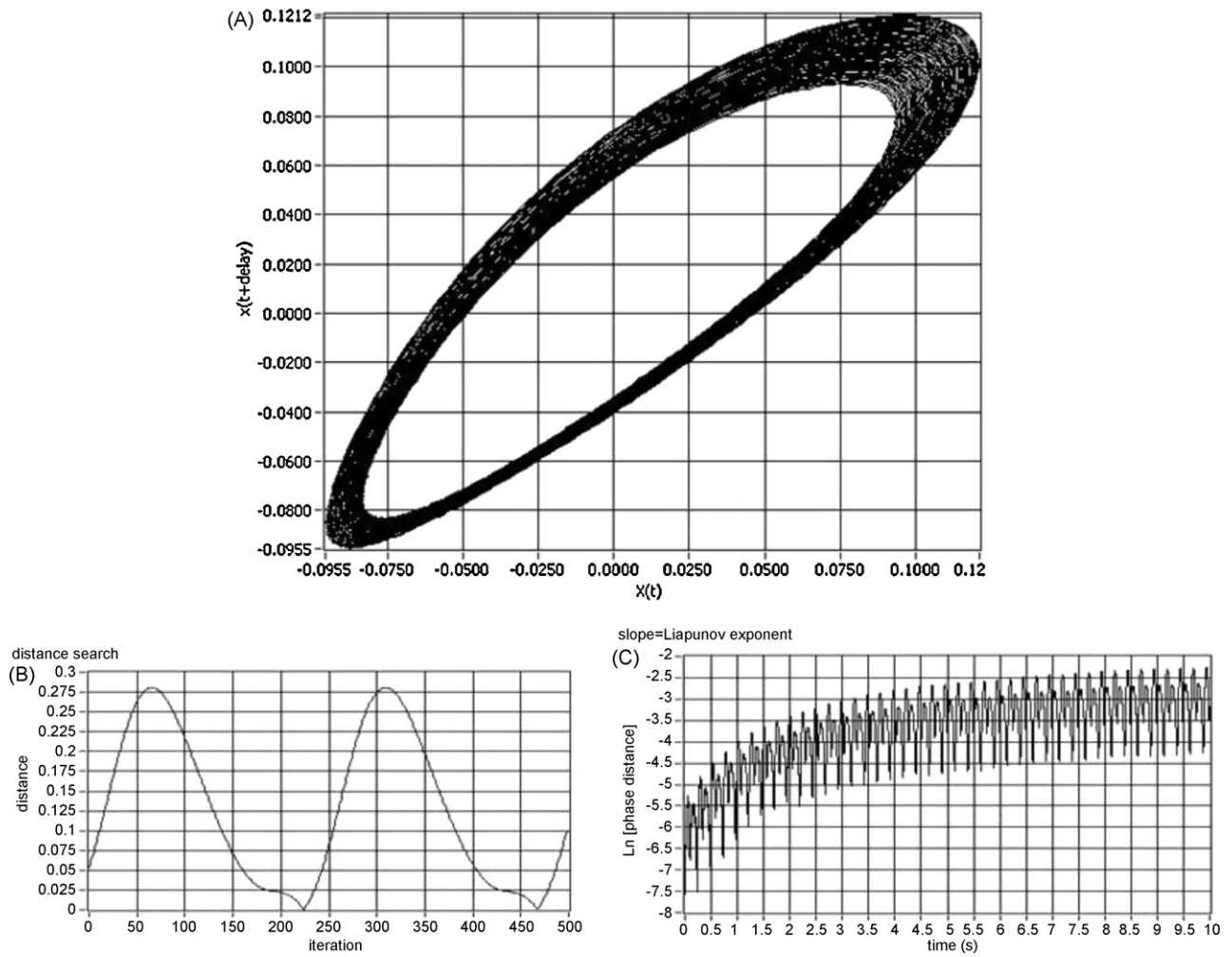


Fig. 10. Lyapunov Exponent and phase space distance graphs of invoked dynamics within the oxygen evolution region. Panel A shows the two-dimensional phase space of the attractor. Panel B is used to find the iteration where the trajectory comes to an infinitesimally close distance from its starting position, representing the period of oscillation. This information is used in panel C which tracks the distance between two infinitesimally close points from two separate trajectories plotted on a logarithmic scale as a function of time. The Lyapunov exponent is the slope of this graph.

the last components in the cascaded series that have reached particular relaxation states in their phase space based on the input information.

Several experiments were conducted to present the mapping and associative capabilities of ECS, which demonstrate the information processing power of the system. A set of simple experiments were designed, where response of the system to sinusoidal frequency perturbations was recorded. These experiments demonstrate the ability of the system to respond to simple and reproducible perturbations in a nonlinear manner with distinct characterizing features. Sinusoidal signals, aside from their simplicity and reproducibility which suit the purposes and the scope of this work, represent a simplified version of most practical signals; they may also be combined in a linear fashion or in a Fourier series to reconstruct more complex information sets.

After adjusting the experimental parameters to bring the system into a responsive region and upon stimulation with sinusoidal frequency perturbations, the response was both reproducible and complex, exhibiting quasi-periodic patterns, frequency drift and phase oscillations.

In order to characterize phase synchronization, the analytic signal approach based on the Hilbert transform was used (Rosenblum et al., 1996). The Hilbert's transform of a function $x(t)$ can be defined

as follows:

$$h(t) = H\{x(t)\} = -\frac{1}{\pi} \int_{-\infty}^{\infty} \frac{x(\tau)}{t - \tau} d\tau \quad (4.1)$$

However, this transform was calculated by employing FFT and inverse FFT, since the Fourier transform of $h(t)$ is given by,

$$H(f) = -j \operatorname{sgn}(f) X(f) \quad (4.2)$$

where $H(f)$ and $X(f)$ define the Fourier transforms of $h(t)$ and $x(t)$, respectively. The reverse FFT algorithm can then be applied to obtain $h(t)$. The analytic signal $\Psi(t)$ can be constructed as follows:

$$\Psi(t) = x(t) + jh(t) = A(t)e^{j\Phi(t)} \quad (4.3)$$

From this we define $A(t)$ to be the instantaneous amplitude and $\Phi(t)$ to be the instantaneous phase. The separation of phase and magnitude allows for the use of instantaneous phase as an isolated measurement which contains information about the drift in temporal activity of a particular electrode.

To identify the changing nature of the frequency with respect to time, with a computationally efficient algorithm that can be applied in real time systems, an extension of the instantaneous phase

algorithm was developed. The instantaneous phase plot is first unwrapped to eliminate discontinuities. As the phase is calculated in radians, a full cycle is completed within a 2π period. Since frequency in hertz is measured as periods per seconds, the instantaneous frequency can then be calculated by taking the derivative of spectrum in time, and scaling this by 2π . That is, instantaneous frequency f_{ins} , is given as follows:

$$f_{\text{inst}} = \frac{d\phi(t)}{dt} \frac{1}{2\pi} \quad (4.4)$$

Instantaneous frequency analysis is useful for looking at response patterns generated from perturbations in the passivation region during electrochemical dissolution of nickel. An example of frequency band response, spanning a spectrum of approximately 10 Hz in response to a simple oscillatory stimulus is presented in Fig. 8A. The frequency drift observed in Fig. 8B is a clear indication of the non-triviality of the system response, stimulated by the perturbation. These drifts are likely related to the motion and acceleration of spatial fronts which have been reported in electrochemical experiments (Lev et al., 1990; Krischer et al., 2001) and general nonequilibrium systems (Coullet, 2002).

Fig. 9 is an example of slower response patterns which were generated by the nickel electrodisolution system in the oxygen evolution region. The effect of a 5 s stimulation coming on at 4 s in Fig. 9A is noticeable in the raw data. The subsequent transformations in the temporal dynamics resulting from this perturbation are significant and visible from the distinct frequency bands in the power spectrum of Fig. 9B which form following the application of the perturbation. The response is a dynamic band between 4 and 5 Hz, with frequencies up to several harmonics present in the spectrum analysis. As with the response in the passivation region, the frequency of the system response is not static in time and higher harmonics occupy a wider band, which is indicative of the larger frequency drift in these components.

The reconstruction of the phase plot of the system response shown in two-dimensional space is illustrated in Fig. 10. The phase plot signifies a low dimensional attractor structure which follows the application of perturbation. Although the localized phase space structure occupies only a portion of the phase space in 2D, it is not a simple oscillatory system. To better characterize the dynamics an algorithm was implemented to calculate the largest Lyapunov exponent. The exponent is a measure of rate of separation of infinitesimally close trajectories:

$$|d(t)| = e^{\lambda t} |d(0)| \quad (4.5)$$

For λ representing the Lyapunov exponent, $d(0)$ the infinitesimally small initial separation and $d(t)$ the separation of trajectories after time (t). The largest Lyapunov exponent can be calculated as follows:

$$\lambda = \lim_{t \rightarrow \infty} \frac{1}{t} \ln \left| \frac{d(t)}{d(0)} \right| \quad (4.6)$$

Fig. 10 is an example of strange attractor dynamics in the system response where it can be clearly seen that there is a positive Lyapunov exponent. Such attractor dynamics allow for a level of abstraction which can segment a large variety of external world information into a few significant categories, while at the same they can store information and exhibit a memory function through their information dimension.

5. Conclusions

Pattern formation enables the brain to predict and classify phenomena based on stored internal models which are associated with particular sensory information. This form of information processing

allows for recognition from incomplete data due to the representation of information in form of abstractions that are mapped to a whole category of observations from the external world.

Many nonlinear dynamical systems that operate far from equilibrium exhibit interesting emergent patterns which can form and evolve in response to various parameters that affect them. Formation of such patterns can be looked at as a mechanism of recognition, response and memory in form of the dynamics of emergent patterns. This is a form of distributed information processing taking place in the material.

Electrochemical systems represent the ideal platform to implement the proposed information processing apparatus, in that they satisfy the essential requirements of a material intelligent system. These are the formation of patterns, both spatial and temporal within a reasonable and yet detectable time frame, their ease of implementation, and demonstrated means of interaction and control. Electrochemical systems have an impressive range of spatial and temporal dynamics spanning from chaos to orderly regimes and transitions in the phase dynamics. Furthermore, we have shown that these patterns can be evoked with distinct perturbations and control parameters, effectively forming an associative memory system. It is likely that in the coming decades a new age of computer technology will emerge that is based on pattern formation inside complex systems.

References

- Amit, D.J., 1989. *Modelling Brain Function: The World of Attractor Neural Networks*. Cambridge University Press, New York.
- Barlow, H., 1990. The mechanical mind. *Annual Review of Neuroscience* 13, 15–24.
- Bertram, M., Mikhailov, A.S., 2001. Pattern formation in a surface chemical reaction with global delayed feedback. *Physical Review E* 6306 (6), art. no.-066102.
- Bertram, M., Mikhailov, A.S., 2003. Pattern formation on the edge of chaos: mathematical modeling of CO oxidation on a Pt(110) surface under global delayed feedback. *Physical Review E* 67 (3).
- Burke, J., Knobloch, E., 2006. Localized states in the generalized Swift–Hohenberg equation. *Physical Review E* 73 (5).
- Christoph, J., Eismir, M., 2002. Theory of electrochemical pattern formation. *Chaos* 12 (1), 215–230.
- Coullet, P., 2002. Localized patterns and fronts in nonequilibrium systems. *International Journal of Bifurcation and Chaos* 12 (11), 2445–2457.
- Coullet, P., Riera, C., et al., 2004a. A new approach to data storage using localized structures. *Chaos* 14 (1), 193–198.
- Coullet, P., Toniolo, C., et al., 2004b. How much information can one store in a nonequilibrium medium? *Chaos* 14 (3), 839–844.
- Cross, M.C., Hohenberg, P.C., 1993. Pattern-formation outside of equilibrium. *Reviews of Modern Physics* 65 (3), 851–1112.
- Crutchfield, J.P., 1994. The calculi of emergence—computation, dynamics and induction. *Physica D* 75 (1–3), 11–54.
- Crutchfield, J.P., Mitchell, M., 1995. The evolution of emergent computation. *Proceedings of the National Academy of Sciences of the United States of America* 92 (23), 10742–10746.
- De Wit, A., 1999. Spatial patterns and spatiotemporal dynamics in chemical systems. *Advances in Chemical Physics* 109, 435–513.
- Delgado, J., Sole, R.V., 1997. Collective-induced computation. *Physical Review E* 55 (3), 2338–2344.
- Eckmann, J.P., Ruelle, D., 1985. Ergodic-theory of chaos and strange attractors. *Reviews of Modern Physics* 57 (3), 617–656.
- Ertl, G., 1991. Oscillatory kinetics and spatiotemporal self-organization in reactions at solid-surfaces. *Science* 254 (5039), 1750–1755.
- Ertl, G., 2002. Dynamics of surface reactions. *Faraday Discussions* 121, 1–15.
- Flaaten, G., Krischer, K., 1995. A general-model for pattern-formation in electrode-reactions. *Journal of Chemical Physics* 103 (13), 5428–5436.
- Frank, U., 1978. Chemical oscillations. *Angewandte Chemie-International Edition in English* 17 (1), 1–15.
- Fraser, A.M., Swinney, H.L., 1986. Independent coordinates for strange attractors from mutual information. *Physical Review A* 33 (2), pp. 1134 LP–1140.
- Gollub, J.P., Langer, J.S., 1999. Pattern formation in nonequilibrium physics. *Reviews of Modern Physics* 71 (2), S396–S403.
- Grassberger, P., Procaccia, I., 1983. Characterization of strange attractors. *Physical Review Letters* 50 (5), 346–349.
- Haken, H., 1996. *Principles of Brain Functioning: A Synergetic Approach to Brain Activity, Behavior and Cognition*. Springer, Berlin, New York.
- Haken, H., 2002. *Brain Dynamics: Synchronization and Activity Patterns in Pulse-coupled Neural Nets with Delays and Noise*. Springer, Berlin, New York.
- Haken, H., 2004. *Synergetic Computers and Cognition: A Top-down Approach to Neural Nets*. Springer-Verlag, Berlin, New York.

- Haken, H., 2006. Synergetics of brain function. *International Journal of Psychophysiology* 60 (2), 110–124.
- Hopfield, J.J., 1982. Neural networks and physical systems with emergent collective computational abilities. *Proceedings of the National Academy of Sciences of the United States of America: Biological Sciences* 79 (8), 2554–2558.
- Hudson, J.L., Bassett, M.R., 1991. Oscillatory electrodisolution of metals. *Reviews in Chemical Engineering* 7 (2), 109–170.
- Jaeger, N.I., Otterstedt, R.D., et al., 2002. Evolution of spatiotemporal patterns during the electrodisolution of metals: experiments and simulations. *Chaos* 12 (1), 231–239.
- Kiss, I.Z., Kazsu, Z., et al., 2006. Tracking unstable steady states and periodic orbits of oscillatory and chaotic electrochemical systems using delayed feedback control. *Chaos* 16 (3).
- Kiss, I.Z., Wang, W., et al., 1999. Experiments on arrays of globally coupled periodic electrochemical oscillators. *Journal of Physical Chemistry B* 103 (51), 11433–11444.
- Kiss, L., 1988. *Kinetics of Electrochemical Metal Dissolution*. Elsevier, Amsterdam, New York.
- Koch, A.J., Meinhardt, H., 1994. Biological pattern-formation—from basic mechanisms to complex structures. *Reviews of Modern Physics* 66 (4), 1481–1507.
- Kohonen, T., 1989. *Self-organization and Associative Memory*. Springer-Verlag, Berlin, New York.
- Koper, M.T.M., 1998. Non-linear phenomena in electrochemical systems. *Journal of the Chemical Society-Faraday Transactions* 94 (10), 1369–1378.
- Krischer, K., 2001. New directions and challenges in electrochemistry—spontaneous formation of spatiotemporal patterns at the electrode vertical bar electrolyte interface. *Journal of Electroanalytical Chemistry* 501 (1–2), 1–21.
- Krischer, K., Lubke, M., et al., 1991. Chaos and interior crisis in an electrochemical reaction. *Berichte Der Bunsen-Gesellschaft: Physical Chemistry Chemical Physics* 95 (7), 820–823.
- Krischer, K., Mazouz, N., et al., 2000. Pattern formation in globally coupled electrochemical systems with an S-shaped current–potential curve. *Journal of Physical Chemistry B* 104 (31), 7545–7553.
- Krischer, K., Mazouz, N., et al., 2001. Fronts, waves, and stationary patterns in electrochemical systems. *Angewandte Chemie-International Edition* 40 (5), 851–869.
- Lev, O., Sheintuch, M., et al., 1990. Spatial current distribution during nickel anodic dissolution in sulfuric acid. *Chemical Engineering Science* 45 (4), 839–847.
- Lev, O., Wolffberg, A., et al., 1988. Bifurcations to periodic and chaotic motions in anodic nickel dissolution. *Chemical Engineering Science* 43 (6), 1339–1353.
- Levart, E., Schuhman, D., 1970. Migration–diffusion coupling and concept of electrochemical impedance. *Journal of Electroanalytical Chemistry* 24 (1), 41–48.
- Lin, A.L., Hagberg, A., et al., 2000. Four-phase patterns in forced oscillatory systems. *Physical Review E* 62 (3), 3790–3798.
- Maselko, J., 2003. Pattern formations in chemical systems. *Advances in Complex Systems* 6 (1), 3–14.
- Mazouz, N., Flatgen, G., et al., 1997. Tuning the range of spatial coupling in electrochemical systems: from local via nonlocal to global coupling. *Physical Review E* 55 (3), 2260–2266.
- Mazouz, N., Krischer, K., 2000. A theoretical study on turing patterns in electrochemical systems. *Journal of Physical Chemistry B* 104 (25), 6081–6090.
- Nicolis, G., Prigogine, I., 1977. *Self-organization in Nonequilibrium System: From Dissipative Structures to Order through Fluctuations*. Wiley, New York.
- Nicolis, J.S., 1987. *Chaotic Dynamics Applied to Biological Information Processing*. Akademie-Verlag, Berlin.
- Rosenblum, M.G., Pikovsky, A.S., et al., 1996. Phase synchronization of chaotic oscillators. *Physical Review Letters* 76 (11), 1804–1807.
- Sazou, D., Pagitsas, M., 1991. Periodic and aperiodic current oscillations induced by the presence of chloride-ions during electrodisolution of a cobalt electrode in sulfuric-acid-solutions. *Journal of Electroanalytical Chemistry* 312 (1–2), 185–203.
- Scully, J.R., 1987. Electrochemical methods of corrosion testing. *Corrosion* 13, 213, ASM Inter.
- Turing, A.M., 1952. The chemical basis of morphogenesis. *Philosophical Transactions of the Royal Society of London Series B: Biological Sciences* 237 (641), 37–72.
- Vanag, V.K., Epstein, I.R., 2007. Localized patterns in reaction–diffusion systems. *Chaos* 17 (3).
- Vanderwolf, C.H., 1998. Brain, behavior, and mind: what do we know and what can we know? *Neuroscience and Biobehavioral Reviews* 22 (2), 125–142.
- Yoon, R.S., Borrett, D.S., et al., 1995. Three-dimensional object recognition using a recurrent attractor neural network. *Engineering in Medicine and Biology Society, IEEE 17th Annual Conference*, vol. 1.
- Zhai, Y.M., Kiss, I.Z., et al., 2004. Emerging coherence of oscillating chemical reactions on arrays: experiments and simulations. *Industrial & Engineering Chemistry Research* 43 (2), 315–326.