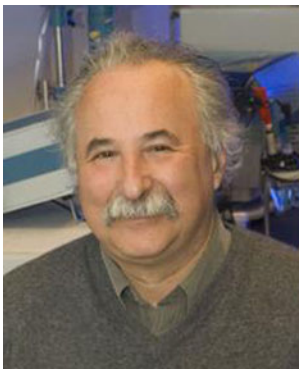
J Solid State Electrochem (2011) 15:1471–1480
DOI 10.1007/s10008-011-1300-4

REVIEW

Processing electrochemical signals at both sides of interface: electronic vs. chemical signal processing

Evgeny Katz

Received: 21 December 2010 / Revised: 29 December 2010 / Accepted: 30 December 2010 / Published online: 19 March 2011



Abstract The paper outlines the development of methods and instrumentation for signal processing in electrochemical systems. Particular attention is given to the transition of the signal processing from an electronic circuitry to molecular information processing systems.

Keywords Electrochemical instrument · Potentiostat · Polarograph · Chemical computing · Biocomputing

Introduction

Processing of electrochemical signals is always considered as a part of an electronic process being performed in an instrumental setup. Therefore, the progress in the signal processing is always associated with the development of the electrochemical instrumentation. Indeed, transition from first electromechanical devices to electronic and later computerized systems made revolutionary changes in the way how electrochemical signals are processed. However, prior to the electronic processing there is a chemical process in a solution or directly at a chemically modified electrode interface. This process can be used to facilitate the electronic signal processing and, in some extent, to substitute the electronic processes with chemical information processing steps. It should be noted that computing and decision-making steps could be performed in chemical systems prior to the electronic process. This paper outlines the progress in the electrochemical signal processing at both sides of the electrode interface: in the electronic part due to designing new electrochemical instruments and in the chemical part due to introduction of novel concepts of unconventional chemical computing. The later one is mostly considered in the form of biochemical logic information processing performed by enzyme systems. The present unusual format of the paper allows a very broud overview of the electrochemistry progress: from the Heyrovský's first polarograph to modern electrochemical instruments, and then from bioelectrochemistry to biocomputing.

E. Katz (✉)
Department of Chemistry and Biomolecular Science,
Clarkson University,
Potsdam, NY 13699-5810, USA
e-mail: ekatz@clarkson.edu

Electronic Side of Interface

Past

Modern electroanalytical chemistry has been started from the invention of polarography by Prof. Jaroslav Heyrovský in 1920s [1–3]. Prior to this invention in 1918–1920, Jaroslav Heyrovský, being still a young scientist, was doing experiments in the laboratory of Prof. Bohumil Kučera [4, 5] on electrocapillarity properties of mercury by weighing mercury drops fallen from a glass capillary connected to a mercury reservoir upon application of a variable potential to the mercury electrode [6]. These experiments were rather

time-consuming because each experimental point for a different potential required collecting many droplets of mercury, their drying and weighing. Then the measured weight was plotted as a function of the applied voltage to obtain the electrocapillarity curve. In order to facilitate the measurements, Heyrovský suggested measuring the time intervals between the mercury drops instead of weighting the collected droplets [7, 8]. Still it was a very tedious work to obtain the whole curve. A real breakthrough was achieved in 1921 when Heyrovský applied current measurements on a dropping mercury electrode (DME) instead of measuring the weight or time dependences. Still in the beginning, the current measurements were performed separately for each applied potential value (Fig. 1, left) and then plotted manually as current vs. potential curves (Fig. 1, right). The method became the first electroanalytical technique—polarography [9–11] in 1924 when Prof. Heyrovský together with his research assistant Masuzo Shikata [12] designed an instrument for automatic recording of current upon linearly increasing voltage applied between a dropping mercury electrode and a counter electrode [13] (Fig. 2, left). In this very first electrochemical instrument (Fig. 2, right), voltage applied to the electrochemical cell (D) was supplied from a storage battery (H) with a linearly increasing value using a potentiometric bridge (B) controlled by an electric motor (A). A light beam produced by a galvanometer lamp (G) was reflected by a galvanometer mirror (E) to be recorded on a photographic paper (C) which rotation was synchronized with the rotation of the potentiometric bridge. A shunt (F) allowed sensitivity control of the galvanometer. Application of this instrument was a big step towards electronic transduction of electrochemical signals [14–18]. The first prototype instrument invented by Heyrovský–Shikata after appropriate engineering became commercially available for electrochemical polarographic studies. One of the first commercial models with photographically recorded current vs. voltage curves is shown in Fig. 3.

Rapid developments in electronic instruments after WWII resulted in new advanced electrochemical instruments. Designing an electronic potentiostat by A. Hickling [19] later improved by Hans Wenking [20] in 1950s was an important contribution to the development of electrochemical instruments. In new instruments, in addition to the advanced potentiostatic control during the measurements, the electronic signal was recorded by a pen on paper excluding the need of the photographic paper processing. A few example models of recording polarographs [21–25] are shown in Fig. 4. These instruments resulted in significant simplification of the electrochemical analysis allowing recording of polarograms (current vs. potential dependences measured on a DME) in minutes rather than hours as it was earlier with the photographic paper. These instruments were in use for several decades till 1980s [26]. While doing my first electrochemical studies as a PhD student [27, 28], I was using a recording polarograph, model OH-102, Radelkis, Hungary (Fig. 5). Still the experiments had to be well-planned to allow convenient data presentation. For example, a set of polarograms recorded with different concentrations should be measured with sensitivity which allows all curves to be placed on the same plot (the problem which does not appear in modern computerized instruments where rescaling of experimental curves is very simple). A new generation of young researchers cannot even imagine difficulties in the signal processing which were normal routine in electrochemical studies before computers became available!

In order to record fast changes in electrochemical signals (e.g., upon rapid potential scans), electrochemical instruments were connected to oscilloscopes. So called, oscillopolarographs [29, 30] (Fig. 6) allowed electrochemical measurements on a single mercury droplet during its lifetime. One of the first commercial oscillopolarographs "Polaroscope P-576" was design by J. Heyrovský and J. Forejt [29] and constructed by V. Nessl (Fig. 6, left). Oscillopolarographs were mostly used to analyze electrochemical kinetics (reversibility of electrochemical reactions) and to see unstable intermediate products of primary electrochemical reactions. The traces visualized with a cathode ray oscilloscope were still archived using a photo camera or even copied manually from a screen with a pen on transparent paper.

Present

A new era of computer-controlled electronic devices brought a novel kind of electronic electrochemical instruments with digital signal processing. These instruments can be presently found in every electrochemical laboratory (Fig. 7). Computer-controlled electrochemical instruments allow many different techniques (e.g., cyclic voltammetry, differential pulse voltammetry, chronoamperometry, etc.) [31, 32]. Even more importantly, they allow easy processing of the obtained data which can be rescaled, presented in various plots and analyzed. These extremely powerful instruments allow very fast and easy accumulation of electrochemical data sometimes diminishing the need of careful planning of experiments which was a must for less-advanced instruments. Thinking after experiments rather than before them became unfortunately a bad habit for some students and young researchers as a drawback of the modern "smart" instrumentation. Digital processing of the electrochemical data could also result in overestimation of the precision achievable in electrochemical experiments. Potential values presented with a precision of a fraction of millivolt (e.g., −542.5 mV [33]), which is obviously not achievable, could be found in the modern literature. Despite

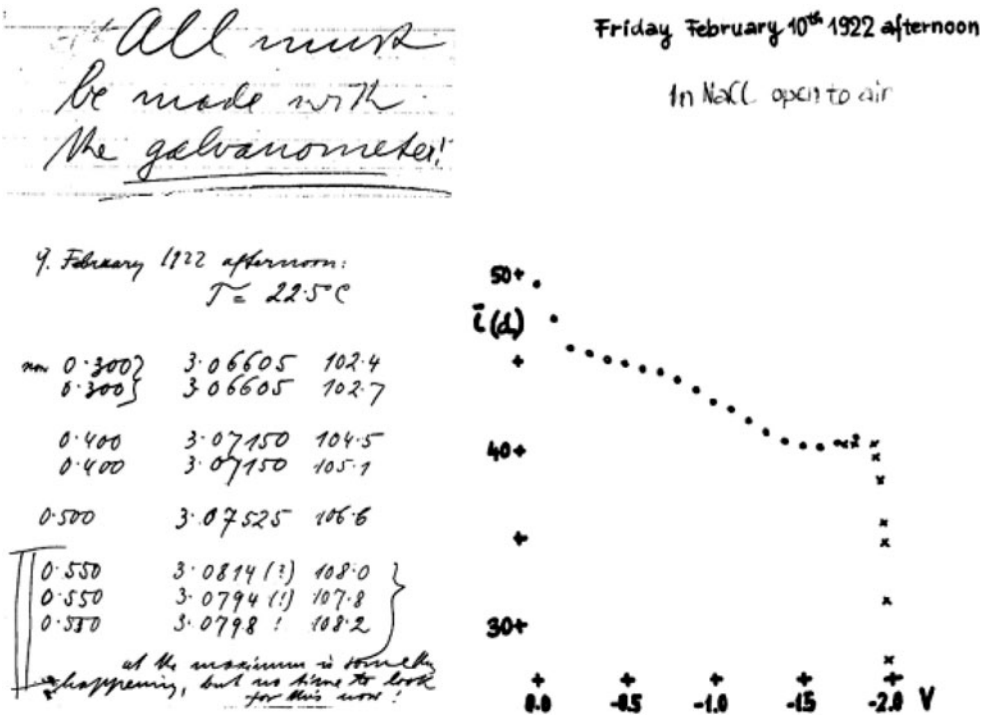


Fig. 1 Two pages from the Heyrovský's laboratory journal from February 9–10, 1922. They show results of point-by-point current measurements at variable potentials (*left*) and manual plotting the results in the form of a current vs. voltage graph (*right*; courtesy of Heyrovský Institute of Physical Chemistry, Prague)

possible over-interpretation of the electrochemical data, the simplicity in the operation of the modern electrochemical instrumentation resulted in broadening of applications of electroanalytical methods. Miniaturization of modern electronic devices allowed electroanalytical instruments of a very small size which can be still enough to accommodate logic devices for the analysis of the electrochemical data in addition to the measuring circuitry (Fig. 8) [34].

Future

Future instruments processing electrochemical data (as well as any other analytical instruments) should be even "smarter" and easier in operation comparing with the present computerized systems. They might be controlled by voice and the programing/data analysis could be intuitive. For example, an operator could ask the intrument "to analyze the potential

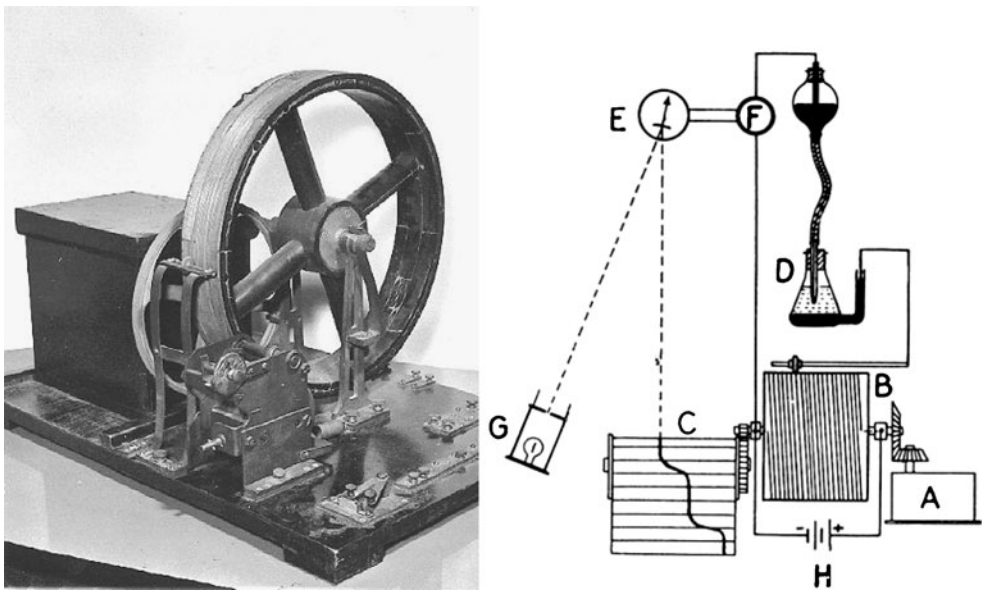


Fig. 2 The very first original polarograph of J. Heyrovský and M. Shikata, 1924 (*left*). The principle of the first Heyrovský–Shikata polarograph (*right*); see the text for the explanation (Courtesy of Heyrovský Institute of Physical Chemistry, Prague)

Fig. 3 Sargent–Heyrovský photographically recorded polarograph Model XII manufactured by EH Sargent and Co., Chicago (Courtesy of ACS)

scan-rate dependence of a cyclic voltammetry response and derive an electron transfer rate constant". Then the instrument will perform the measurements and give the answer automatically using the built-in program. Eventually, this kind of "smart" instrument performance is already possible at the present level of technology. Steping forward to the next level of the computer technology, we may expect direct integration of human brain with electronic computers based on a novel (not available yet) biocomputing platform (Fig. 9, right) substituting the present communication between an operator and computer using a keyboard and mouse (Fig. 9, left) [35]. However, this futuristic vision is much broader than specific applications in the electrochemical instrumentation—it will result in revolutionary transformation of all aspects of human life.

Chemical Side of Interface

Past–Present

Electrochemical analysis of species which cannot be directly reduced/oxidized at an electrode and need to be chemically processed prior to an electrochemical reaction is the major problem in many electrochemical sensors/biosensors. To be more specific, we can consider enzyme-based electrochemical biosensors as an example where a primary analyte (e.g., glucose) needs to be converted by an enzyme reaction to redox species communicating with an electrode. This might include direct communication between enzyme active centers and electrodes (Fig. 10a) or production of redox species upon a natural biocatalytic reaction (e.g., formation of H_2O_2 upon oxidation of glucose by oxygen biocatalyzed by glucose oxidase enzyme; Fig. 10b). Alternatively, artificial electron transfer mediators could be involved in the biocatalytic process to substitute the primary non-electrochemically active analyte with a redox active mediator upon an enzyme-catalyzed reaction. Then the biocatalytically generated mediator provides an electrochemical response which cannot be directly obtained from the primary analyte (Fig. 11). The direct [36] and mediated [37–39] communication of enzymes with electrodes was studied in details in the last two decades enabling many biocatalytic systems applied in various electrochemical biosensors [40] and biofuel cells [41]. The common feature of all studied systems is processing of the primary chemical signal through chemical/biochemical reactions prior to the electrochemical electron transfer step.

Present–Future

Molecular [42–48] and biomolecular [49–51] systems mimicking Boolean logic gates and their networks processing chemical input signals similarly to computers received high attention and were rapidly developed in the last decade. Being a subarea of unconventional computing [52, 53], they can process chemical information mimicking Boolean logic operations using binary definitions (1,0; YES/NO) for high and low concentrations of reacting species separated by a threshold. Using this approach,

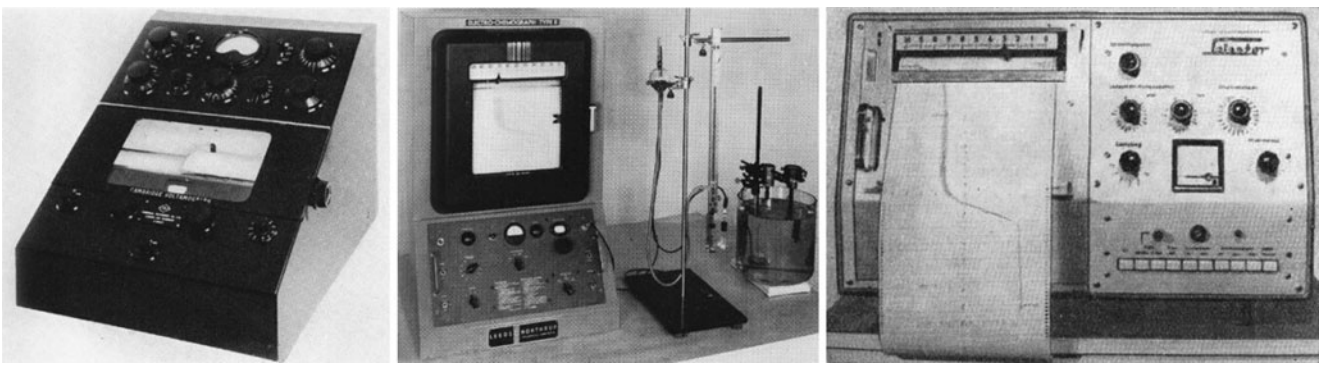


Fig. 4 Recording polarographs: visible recording polarograph "Voltamograph", Cambridge Instrument Co., UK (*left*). Polarograph "Electrochemograph", Type E, manufactured by Leeds & Northrup Co., North Wales, PA, USA (*middle*). Visible recording tast-polarograph "Selector-D", Atlas-Werke, Bremen, Germany (*right*; courtesy of ACS)

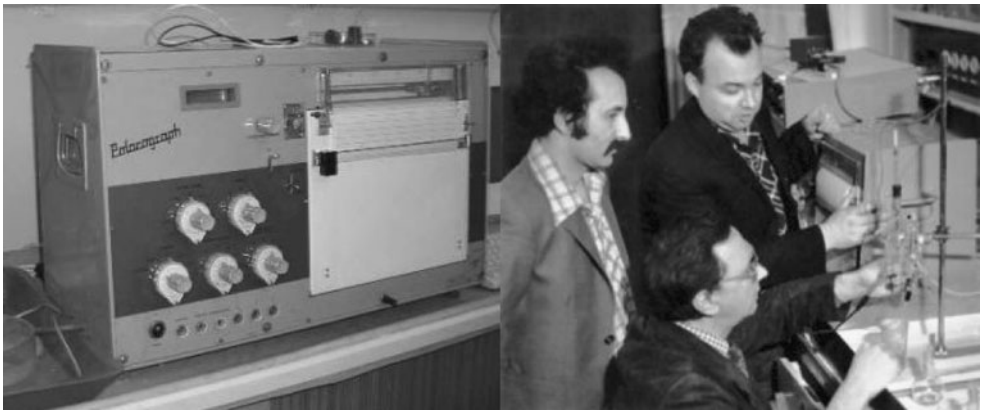


Fig. 5 Recording polarograph, Model OH-102, Radelkis, Hungary. This polarograph allowed normal and derivative modes of polarography. PhD student Evgeny Katz (standing, *left*), Dr. Yuriy Kozlov (standing, *right*) and Prof. Boris Kiselev (*sitting*) performing measurements with Polarograph OH-102 (Institute of Photosynthesis, Russian Academy of Sciences, Pushchino, 1977)

chemical reactions could be reformulated as information processing steps with built-in logic operations [54]. Then, the chemical processes could be programmed similar to computer programming [55, 56] yielding networks performing several logic operations. Based on the recent success in the formulation of logic gates [57–60] and their networks [61] operated by enzyme-catalyzed reactions, systems of various complexities have been designed for processing chemical signals. The enzyme-based logic gates can be arranged in systems similar to electronic integrated circuitries [62]. Theoretical modeling of the enzyme-based logic gates predicts that enzyme logic networks with up to 10 concatenated logic gates should be able to process chemical information within a reasonable noise level [63]. The output signals generated by biomolecular logic gates/networks can be used for switching electrode interfaces between active and inactive states resulting in multi-signal biosensors with the logically processed signals in the chemical part of the systems [64].

pH-Switchable materials immobilized on interfaces of electronic/electrochemical transducers (e.g., Si-based chips [65] or conducting electrodes [66–68]) were coupled with enzyme logic systems producing pH changes in solutions as logic responses to input signals. This allowed electronic transduction of the generated output signals, converting the systems into multi-signal biosensors chemically processing various patterns of the input signals using logic "programs" built-in in the enzyme systems. For example, enzyme logic systems mimicking Boolean AND/OR logic operations and producing the output signal in the form of solution pH changes were coupled with charging-discharging organic shells around Au nanoparticles associated with a Si-chip surface [65]. This resulted in the capacitance changes at the modified interface allowing electronic transduction of the biochemical signals processed by the enzyme logic systems. Another approach to the electrochemical transduction of the output signals generated by enzyme logic systems in the form of pH changes was based on the application of polyelectrolyte-modified electrode surfaces [66–68]. Polyelectrolytes covalently bound to electrode surfaces as polymer brushes reveal pH sensitivity allowing control of the electrode interfacial properties by varying pH values.

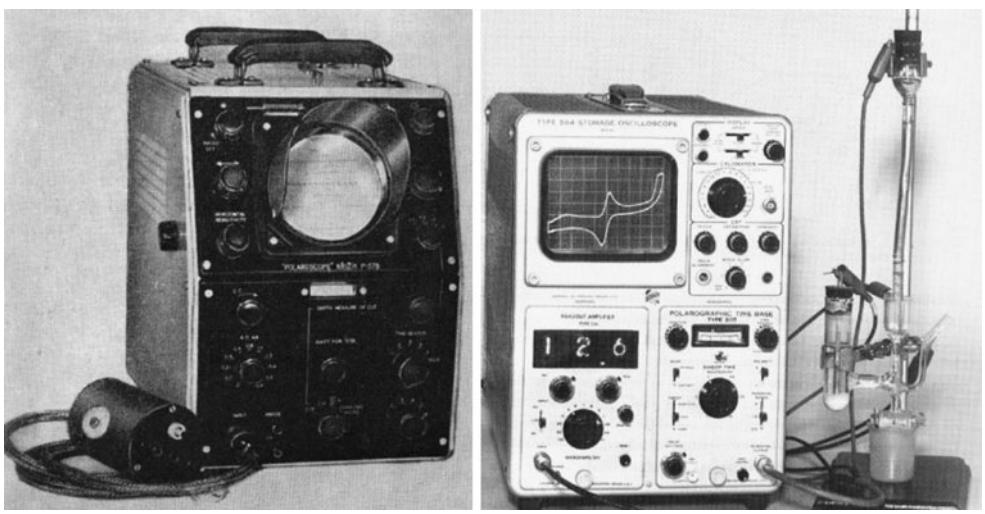


Fig. 6 Oscillopolarographs: Polaroscope P-576, "Zavody prumyslove automatizace", Prague–Smichov (*left*) and Polarographic Analyzer System "Chemtrix" (*right*; courtesy of ACS)

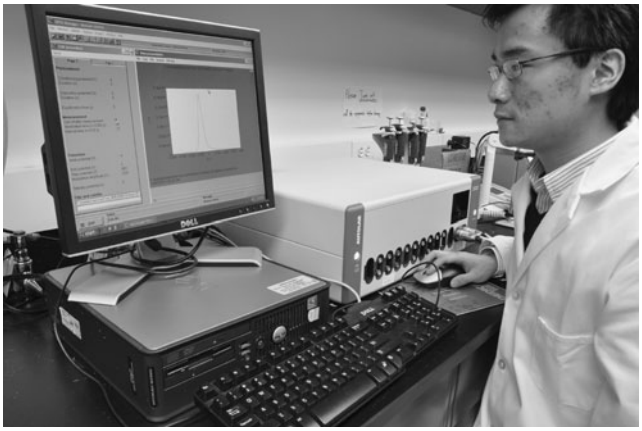


Fig. 7 A computer-controlled electrochemical analyzer (ECO Chemie Autolab PASTAT 10) operated by a PhD student Tsz Kin Tam (laboratory of Prof. Katz, Clarkson University, USA, 2010)

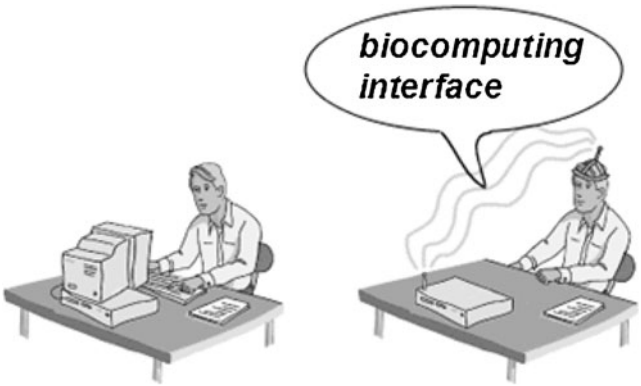


Fig. 9 Communication with a computer using the present keyboard interface (*left*) and futuristic vision of direct communication between an operator brain and an electronic computer through a biocomputing interface (*right*; adopted with permission from [35])

Charged states of the polymer brushes produce hydrophilic swollen thin films on the electrode surfaces resulting in their high permeability for soluble redox probes to the conducting supports, thus yielding the electrochemically active states of the modified electrodes. Upon discharging the polymer chains, the produced hydrophobic shrunken states isolated the conducting supports yielding the inactive states of the modified electrodes. Switching between the ON and OFF states of the electrode modified with the polymer brush was achieved by varying the pH value of the solution. This property of the polymer brush-functionalized electrodes was used to couple them with an enzyme logic system composed of several networked logic gates [68]. The logic network composed of three enzymes (alcohol dehydrogenase, glucose dehydrogenase and glucose oxidase) operating in concert as four concatenated logic gates (AND/OR), was designed to process four different chemical input signals (NADH, acetaldehyde, glucose, and oxygen; Fig. 12). The cascade of biochemical reactions resulted in pH changes controlled by the pattern of the applied biochemical input signals. The "successful" set of the inputs produced gluconic acid as the final product and yielded an acidic medium, lowering the pH of a solution from its initial value of pH 6–7 to the final value of ca. 4, thus switching ON the interface for the redox process of a diffusional redox probe, $[Fe(CN)_6]^{3-/4-}$. The chemical signals processed by the enzyme logic system and

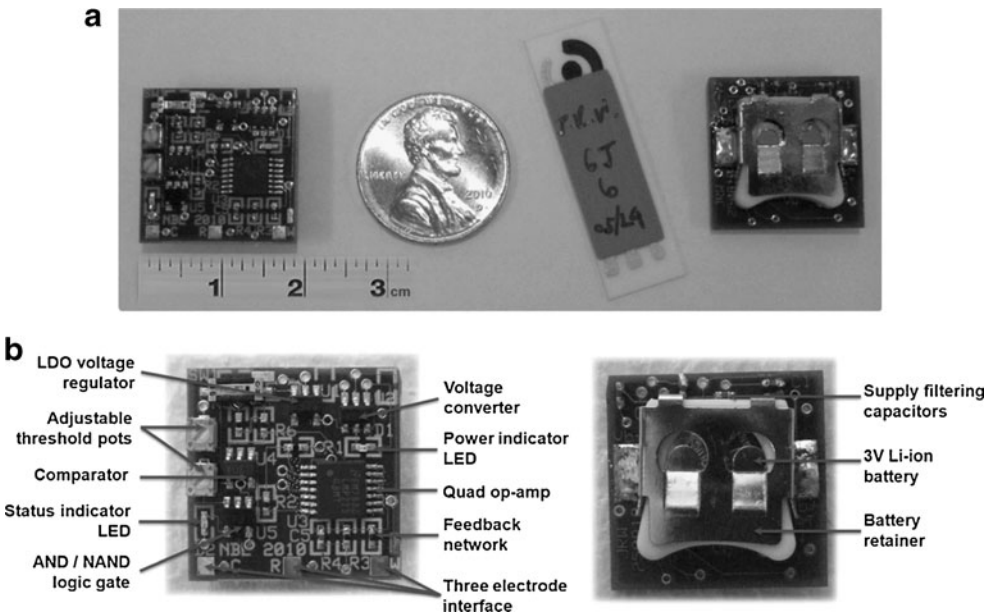


Fig. 8 **a** Image of the microelectronic system (US 1¢ and screen printed three-electrode strip shown for size comparison). **b** Obverse and reverse detail of the microelectronic system indicating the locations of the constituent components on the printed circuit board (adopted with permission from [34])

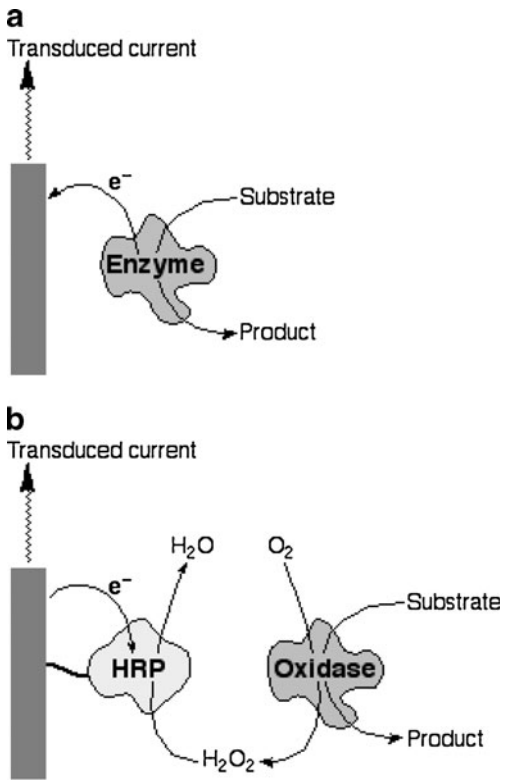


Fig. 10 **a** Direct electron transfer between an enzyme active center and an electrode enabling electrochemical transduction of an analyte (substrate) signal. **b** Electrochemical transduction of an analyte (substrate) signal through intermediate formation of a natural product (H_2O_2) further processed by horseradish peroxidase (HRP) bound to the electrode surface (adopted with permission from [39])

transduced by the sensing interface were read out by electrochemical means using cyclic voltammetry (Fig. 13a). Reversible activation–inactivation of the electrochemical interface was achieved upon logic processing of the biochemical input signals and then by the reset function activated in the presence of urease and urea (Fig. 13a, inset). The whole set of the input signal combinations included 16 variants, while only 0,0,1,1; 0,1,1,1; 1,0,1,1; 1,1,1,0; and 1,1,1,1 combinations resulted in the ON state of the electrochemical interface (Fig. 13b). The present system exemplified a multi-gate/multi-signal processing enzyme logic system associated with an electrochemical transduction read out of the output signal. The electrode interfaces controlled by biomolecular systems logically processing chemical input signals were integrated with various bioelectronic devices, e.g., biofuel cells [69–71] and keypad lock systems [72].

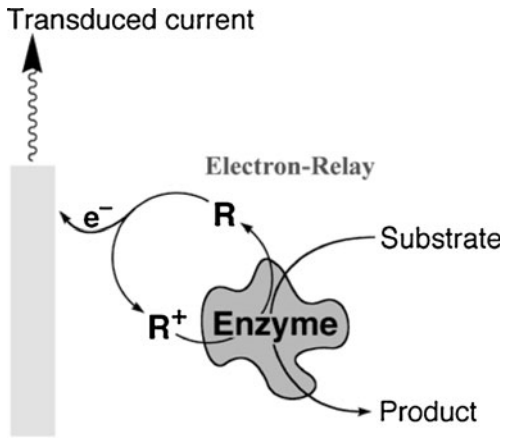


Fig. 11 Mediated transduction of the analyte (substrate) signal upon electron shuttling between the enzyme active center and electrode performed by electron relay species (adopted with permission from [39])

The developed approach paves the way to the novel digital biosensors and bioelectronic devices processing multiple-biochemical input signals and producing a combination of output signals dependent on the whole pattern of various input signals. The biochemical signals are processed by chemical means based on the enzyme logic system prior to their electronic transduction; hence, obviating the need for computer analysis of the biosensing information. We anticipate that biochemical logic gates and networks connected with bioelectronic sensing and actuating devices will find numerous biomedical applications. They will facilitate decision making in connection to an autonomous feedback-loop drug delivery system and will revolutionize the monitoring and treatment of patients. The designed systems exemplify the novel approach to multi-signal processing biosensors [64] mimicking natural biochemical pathways and operating according to the biocomputing concept [49]. Further studies will be needed to transfer this approach from a conceptual demonstration to real-life biosensor applications. This will require a lot of scientific and engineering work to integrate multi-enzyme systems in a rational design with modified electrodes before a real practically applicable biosensor becomes possible. Particularly important will be the operation of the switchable bioelectronic interfaces upon local pH changes without affecting the bulk solution composition [73]. It is interesting to note that the information processing in these bioelectronic devices has moved from the electronic domain to the chemical part being at another side of the electrode interface. The broadening of the possible applications of this concept will result in the design of various bioelectronic/bioelectrochemical devices and bioactuators controlled by complex patterns of multiple inputs.

Conclusions and expectations

As it can be seen from the development of electroanalytical methods and instrumentation, particularly in the recent years, the advances in the signal processing are mostly

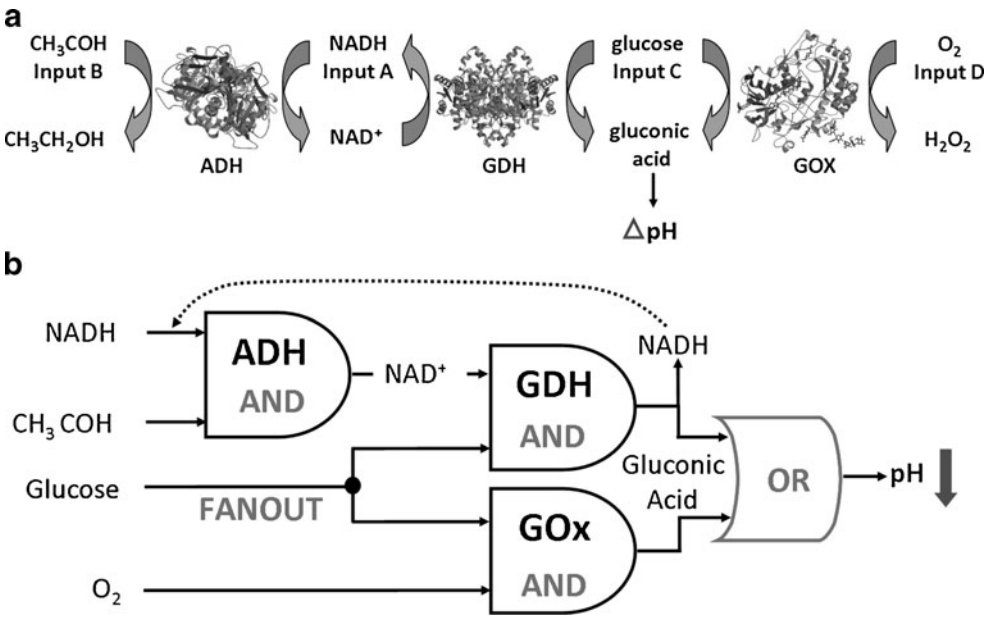


Fig. 12 **a** Multi-gate/multi-signal processing enzyme logic system producing in situ pH changes as the output signal. **b** The equivalent logic circuitry for the biocatalytic cascade (adopted from [68] with permission. Copyright American Chemical Society, 2009)

related to the application of computing technologies which are presently moving from classical electronic devices to unconventional chemical systems. The information processing can be performed at both sides of the electrode interface: at the electronic side as well as in the chemical systems. Obviously, the electronic computers which were progressed over several decades are much more advanced comparing with the first examples of molecular and biomolecular information processing systems which appeared only a few years ago. However, the progress in this novel direction might be faster than the development of electrochemical instruments from the first apparatus designed by Heyrovský and Shikata to the modern computerized devices. Eventually, the molecular information processing systems will allow in the future autonomous operation of electronic/electrochemical systems in a biological environment being fully controlled by biochemical signals. Microrobotics and bioimplantable electronic systems are among the most likely applications to benefit from advances in biomolecular computing. Future progress in these areas will depend on the development of novel computing concepts and design of new signal responsive and information processing materials contributing to molecular information technology [74, 75].

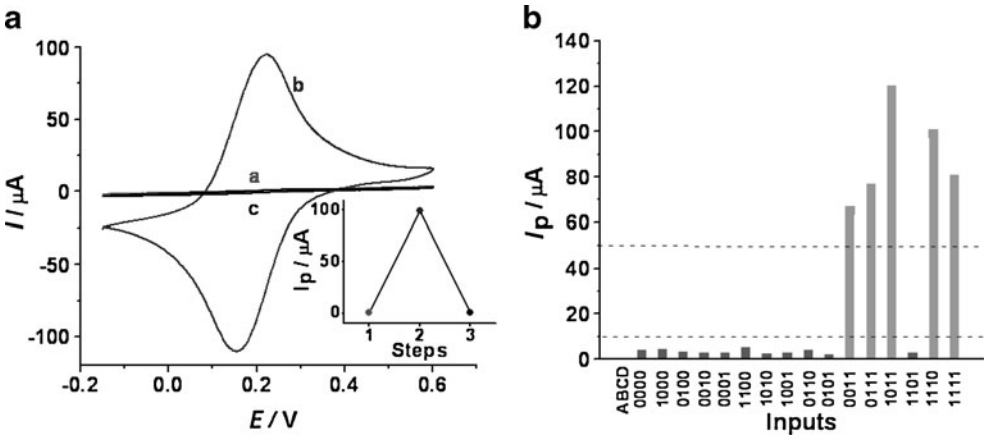


Fig. 13 Electrochemical transduction of the chemical signals processed by the enzyme logic network shown in Fig. 12. **a** Cyclic voltammograms obtained for the ITO electrode modified with the P4VP-polymer brush in **a** the initial OFF state, pH ca. 6.7, **b** ON state enabled by the input combinations resulting in acidifying the solution to pH ca. 4.3, and **c** in situ reset to the OFF state, pH ca. 8.8. *Inset* reversible current changes upon switching the electrode ON-OFF. (**b**) Anodic peak currents, I_p, for the 16 possible input combinations. Inputs A, B, C, D correspond to NADH, acetaldehyde, glucose, and oxygen. The *dotted lines* show threshold values separating logic 1, undefined, and logic 0 output signals (adapted from [68] with permission. Copyright American Chemical Society, 2009)

Acknowledgment This research was supported by the Semiconductor Research Corporation (award 2008-RJ-1839G).

References

1. Zuman P (2001) Crit Rev Anal Chem 31:281
2. Heyrovská R (1998) Curr Sci 74:554
3. Koryta J (1991) Electrochim Acta 36:221
4. Záviška F (1922) Časopis pro pěstování matematiky a fysiky 51:240. Available from: http://dml.cz/bitstream/handle/10338.dmlcz/109017/CasPestMatFys_051-1922-4_3.pdf
5. Boček M (1957) Pokroky matematiky, fyziky a astronomie 2:429. Available from: http://pdf.dml.cz/bitstream/handle/10338.dmlcz/137329/PokrokyMFA_02-1957-4_8.pdf
6. Kučera B (1903) Též Ann d Phys 11:529
7. Heyrovský J (1922) Chemické listy 16:256. Available from: http://electrochem.cwru.edu/estir/hist/hist-22-Heyrovsky-1.pdf
8. Heyrovský J (1923) The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science, Ser. 6, 45:303. Available from: http://electrochem.cwru.edu/estir/hist/hist-23-Heyrovsky-2.pdf
9. Heyrovský J, Kuta J (1966) Principles of polarography. Academic, New York
10. Kolthoff IM, Lingane JJ (1952) Polarography, Interscience, New York (2nd ed).
11. Zutshi K (2006) Introduction to polarography and allied techniques. New Age Intern, New Delhi
12. Osakai T (2008) Shikata, Masuzo. In: Bard AJ, Inzelt G, Scholz F (eds) Electrochemical dictionary. Springer, Berlin, p 607
13. Heyrovský J, Shikata M (1925) Rec Trav Chim 44:496
14. Furman NF, Bricker CE, Whitesell EB (1942) Ind Eng Chem Anal Ed 14:333
15. Abichandani CT, Jatkar SKK (1941) J Ind Inst Sci A23:131
16. Lingane JJ (1946) J Am Chem Soc 68:2448
17. Baumberger JP, Bardwell K (1943) Ind Eng Chem Anal Ed 15:639
18. von Stackelberg M (1950) Polarographische Arbeitsmethoden, de Gruyter, Berlin
19. Hickling A (1942) Trans Faraday Soc 38:27
20. Dölling R (1998) Mater Corros 49:535
21. Whitnack GC (1948) Anal Chem 20:658
22. Allsopp WE, Damerell VR (1949) Anal Chem 21:677
23. Lykken L, Pompeo DJ, Weaver JR (1945) Ind Eng Chem Anal Ed 17:724
24. Lingane JJ (1949) Anal Chem 21:45
25. Schulman JH, Battey HB, Jelatis DG (1947) Rev Sci Inst 18:226
26. Bond AM (1980) Modern polarographic methods in analytical chemistry. Marcel Dekker, New York
27. Kozlov YN, Katz E, Kiselev BA, Evstigneev VB (1979) Biofizika 24:583 (Chemical Abstract: 91:154454s, 1979).
28. Katz E, Kozlov YN, Kiselev BA (1981) Energy Convers Manag 21:171
29. Heyrovský J, Forejt J (1943) Z Phys Chem 193:77
30. Snowden FC, Page HT (1950) Anal Chem 22:969
31. Scholz F (ed) (2010) Electroanalytical methods. Springer, Berlin
32. Wang J (2006) Analytical electrochemistry. Wiley, Hoboken, New Jersey
33. Dytrtová JJ, Jakl M, Šestáková I, Navrátil T, Tlustoš P (2008) Chem Listy 102:s100
34. Windmiller JR, Santhosh P, Katz E, Wang J (2011) Sens Actuat B. in press doi:10.1016/j.snb.2010.11.048
35. Willner I, Katz E (2005) In: Bioelectronics: from theory to applications. Willner I, Katz E (eds). Wiley: Weinheim, Germany, Chapter 15, pp. 457–461
36. Ghindilis AL, Atanasov P, Wilkins E (1997) Electroanalysis 9:661
37. Katz E, Shipway AN, Willner I (2002) In: Encyclopedia of Electrochemistry, Vol. 9: Bioelectrochemistry, G.S. Wilson, (ed), Wiley: Weinheim, Germany, Chapter 17, pp. 559–626
38. Willner I, Katz E (2000) Angew Chem Int Ed 39:1180
39. Katz E, Shipway AN, Willner I (2001) Electron transfer in chemistry. Vol. 4: heterogeneous systems, solid state systems, gas phase systems. In: Balzani V, Piotrowiak P, Rodgers MAJ (eds) Section 1: catalysis of electron transfer. Wiley, Weinheim, Germany, pp 127–201
40. Willner I, Katz E, Willner B (2000) In: Biosensors and their applications, V.C. Yang and T.T. Ngo (eds), Kluwer Academic Publishers, New York, Chapter 4, pp. 47–98
41. Cracknell JA, Vincent KA, Armstrong FA (2008) Chem Rev 108:2439
42. De Silva AP, Uchiyama S, Vance TP, Wannalerse B (2007) Coord Chem Rev 251:1623
43. De Silva AP, Uchiyama S (2007) Nat Nanotechnol 2:399
44. Szacilowski K (2008) Chem Rev 108:3481
45. Credi A (2007) Angew Chem Int Ed 46:5472
46. Pischel U (2007) Angew Chem Int Ed 46:4026
47. Pischel U (2010) Austral J Chem 63:148
48. Andreasson J, Pischel U (2010) Chem Soc Rev 39:174
49. Katz E, Privman V (2010) Chem Soc Rev 39:1835
50. Saghatelian A, Volcker NH, Guckian KM, Lin VSY, Ghadiri MR (2003) J Am Chem Soc 125:346
51. Ashkenasy G, Ghadiri MR (2004) J Am Chem Soc 126:11140
52. Calude CS, Costa JF, Dershowitz N, Freire E, Rozenberg G (eds) (2009) Unconventional computation. Lecture Notes in Computer Science. Vol. 5715, Springer, Berlin
53. Adamatzky A, De Lacy CB, Bull L, Stepney S, Teuscher C (eds) (2007) Unconventional computing. Luniver Press, UK
54. Arugula MA, Halámek J, Katz E, Melnikov D, Pita M, Privman V, Strack G (2009) IEEE Comp. Soc. Publ. (Los Alamitos, California), 1–7.
55. Van Noort D (2005) DNA computing—lecture notes in computer science 3384:365
56. Reif JH, Sahu S (2009) Theor Comp Sci 410:1428
57. Strack G, Pita M, Ornatska M, Katz E (2008) ChemBioChem 9:1260
58. Privman V, Zhou J, Halámek J, Katz J (2010) J Phys Chem B 114:13601
59. Melnikov D, Strack G, Zhou J, Windmiller JR, Halámek J, Bocharova V, Chuang M-C, Santhosh P, Privman V, Wang J, Katz E (2010) J Phys Chem B 114:12166
60. Privman V, Pedrosa V, Melnikov D, Pita M, Simonian A, Katz E (2009) Biosens Bioelectron 25:695
61. Privman V, Arugula MA, Halámek J, Pita M, Katz E (2009) J Phys Chem B 113:5301
62. Zhou J, Arugula MA, Halámek J, Pita M, Katz E (2009) J Phys Chem B 113:16065
63. Privman V, Strack G, Solenov D, Pita M, Katz E (2008) J Phys Chem B 112:11777
64. Wang J, Katz E (2010) Anal Bioanal Chem 398:1591
65. Krämer M, Pita M, Zhou J, Ornatska M, Poghossian A, Schöning MJ, Katz E (2009) J Phys Chem B 113:2573
66. Zhou J, Tam TK, Pita M, Ornatska M, Minko S, Katz E (2009) ACS Appl Mater Interfaces 1:144
67. Wang X, Zhou J, Tam TK, Katz E, Pita M (2009) Bioelectrochemistry 77:69

68. Privman M, Tam TK, Pita M, Katz E (2009) J Am Chem Soc 131:1314
69. Katz E, Pita M (2009) Chem Eur J 15:12554
70. Tam TK, Pita M, Ornatska M, Katz E (2009) Bioelectrochemistry 76:4
71. Amir L, Tam TK, Pita M, Meijler MM, Alfonta L, Katz E (2009) J Am Chem Soc 131:826
72. Halámek J, Tam TK, Strack G, Bocharova V, Katz E (2010) Chem Commun 46:2405
73. Bocharova V, Tam TK, Halámek J, Pita M, Katz E (2010) Chem Commun 46:2088
74. Zauner KP (2005) Crit Rev Solid State Mater Sci 30:33
75. Fu L, Cao LC, Liu YQ, Zhu DB (2004) Adv Colloid Interface Sci 111:133