Developments in Electrochemical Instrumentation

Janet Osteryoung

Summary. Commercial electrochemical instrumentation is in a state of mature development. Microprocessors are used mainly as devices for data handling, and there are no commercial computer-based instruments. Progress in the science and proliferation of applications depend on noninstrumental factors such as electrode materials.

Electrochemistry comprises a diverse group of research areas and technologies. In the United States the academic development of electrochemistry has centered in chemistry departments and has been dominated by the subfield of electroanalytical chemistry (*1*). The main emphasis in this branch of electrochemistry has been on the development of a variety of electrochemical techniques for application to a broad scope of problems not restricted to or even focused on chemical analysis. A major period of development of techniques and associated instrumentation during the late 1950's and the 1960's was successful enough to stimulate a broader use of electrochemistry by nonspecialists.

The immediate impetus for the diffusion of electrochemistry beyond the limited purview of professional electrochemists was the introduction in 1968 of a modern, multipurpose voltammetric instrument [the Princeton Applied Research (PAR) model 170] by what is now EG&G Princeton Applied Research Corporation (*2*). This was quickly followed by the smaller, less flexible, less expensive PAR 174, which became the standard for routine voltammetry (*3*). At the same time, electrochemical techniques became more widely adopted in chemical research (*4*). The commonality of interfacial science attracted biologists to electrochemistry and interested electrochemists in biological problems. The Organoelectric Division of The Electrochemical Society, Inc., changed its name to the Organic and Biological Electrochemistry Division, accurately reflecting a change in emphasis from industrial organic synthesis to a broad view of electrochemical properties of organic substances. This history illustrates a major point: that the term instrumentation generally should be understood to have the connotation commercial instrumentation. There are exceptions, of course: the discerning studies of Hodgkin *et al.* (*5*) on nerve conduction betokened developments in electrochemical theory and instrumentation of the next 20 years. But, in general, new ideas as embodied in new techniques have a broad impact on science and technology only if they are realized in commercial instruments.

On the other hand, the important electrochemical technologies related to batteries, corrosion, electrodeposition, and electrolysis have been much more closely connected with research efforts in electrochemical engineering, where the focus is on design. The considerable competitive advantage conferred by minor improvements in large-scale processes makes most of the work in these areas confidential. Therefore it is difficult to assess the importance of instrumentation or, taking a broader view, electrochemical research to progress in these areas (*6*). However, the main lines of technique and instrumental development appear to have benefited primarily the science of electrochemistry itself, secondarily chemistry in general, and the major electrochemical technologies to a much lesser extent (*7*).

Of course, electrochemical science does contribute to developments in electrochemical technology. Particularly in the understanding of corrosion and passivation of metal surfaces, the contributions can be documented (*8*, volume 4). These contributions have come largely from the European school of physical electrochemistry, which is grounded in the work of Faraday, Nernst, and others (*9*) and which dominates electrochemistry outside the United States. The importance of the science to technologies such as electrochemical processing and energy conversion and storage is less apparent (*8*, volumes 2 and 3). For example, almost all research in electrochemistry is done under conditions of controlled potential, but all industrial electrochemical processing is done at controlled current. In part for this reason, modern techniques for studying electrode processes have not been used widely to support development of electrochemical processes or devices. Thus, although this article is written for the general scientific reader, it may be of some interest as well to electrochemists who are unfamiliar with recent developments in the techniques and instrumentation of electroanalytical chemistry.

In the science of electrochemistry and in its analytical and technological applications, the goal is to control the interface between the electrode of interest and the solution. The interface, or perhaps better, interfacial region, extends from a surface in the electrode where the electrode has its bulk properties to a surface in the solution where the solution has its bulk properties. Precise thermodynamic descriptions of this region exist (*10*) and statistical mechanical models are being developed to aid in investigating its structure (*11*).

The principal motivation for understanding the interface is to understand how its energetics and structure influence electrochemical reactions. The classical example is that of reduction of hydrogen ion in acidic aqueous solutions. The exchange current density (that is, the reaction rate at the potential where the forward and backward rates are the same) is 10^{11} times greater at a platinum electrode than at a mercury electrode (*4*, p. 61). The standard potential is exactly the same in the two cases. This pronounced difference in rate is entirely an interfacial phenomenon. The interface can be controlled to some extent by choice of the three components of the electrochemical experiment: the electrode itself, the solution, and the way in which electrical parameters are controlled in an electrochemical cell incorporated into an electrical circuit.

Inspired choice of solution or electrode material and systematic variation of solution composition to test or develop theories have dominated developments in electrochemistry. Compilations of electrochemical data amply document the importance of these choices in regu-

---

The author is a professor in the Department of Chemistry, State University of New York, Buffalo 14214.

0036-8075/82/1015-0261$01.00/0

lating electrochemical behavior (*12, 13*). The early kinetic studies of L. Gierst and co-workers relied most heavily on variation of salt composition in aqueous solutions to probe the structure of the interface (*10*, chapter 9). From an entirely different point of view, the inspired notion that thionyl chloride could serve as both the oxidant and the solvent has produced a new family of high-energy-density batteries (*14*). And the introduction of the dimensionally stable anode (DSA), which consists of a RuO_2-TiO_2 solid solution coated on titanium metal, has changed significantly the economics of chlorine production (*8*, volume 2, chapter 2). In the future, chemical approaches to electrochemical problems should continue to dominate most areas of application. But the cycle of problem solving that connects research and applications depends critically on the availability of commercial instruments that are suitable for a variety of purposes.

Electrochemical Instrumentation

Electrochemical instrumentation is affected by developments in electronics, through their impact both on direct functions of measurement and control and on computer hardware. In the latter context, the general view of the role of computers in scientific instrumentation presented recently by Enke (*15*) certainly applies to electrochemical instrumentation. Computers have had and will continue to have a profound effect on what experiments we do and how we do them. The reverse is not true. The most insightful and lucid electrochemists have not affected the development of computers or their role in instrumentation. This combination of circumstances makes the subject important but frustrating and invites further discussion.

The role of computers. First consider the computer as a tool for computation. In this role computers have changed the nature of electrochemistry, for they have made it possible to calculate the response to be expected in complex experimental situations not amenable to

Table 1. Selected instruments for electrochemistry

Manufacturer or vendor	Product	Remark
Analytical Measurements	*p*H meters, electrometers*	
Astra Scientific International	Potentiostat, coulometer, voltammetric instruments, *p*H meters, electrometers, conductivity meters, function generators, *p*H and other electrodes, electrochemical HPLC detector, autotitrators, galvanostat	Tacussel
Beckman Instruments	*p*H meters, electrometers (a–e)†, dissolved oxygen (DO) analyzer, autotitrators	
Bioanalytical Systems	*p*H meters, electrometers (a–d), potentiostat (d), electrochemical HPLC detector (d, e)	
Brinkmann Instruments	Voltammetric instruments (e, f), *p*H meters, electrometers (b–e), conductivity meters (b, c) *p*H and other electrodes, electrochemical HPLC detector, autotitrators (d–f)	Metrohm
Chemtrix	*p*H meters, electrometers (a), *p*H electrodes	
Coulometrics	Coulometer, autotitrators (f)	CO_2 determination
Delta Scientific (Xertex)	Chlorine analyzer (d), *p*H meters, electrometers (c), *p*H electrodes, DO analyzer (c)	Process control
ECO	Conductivity meters (b, c), DO analyzer (a), autotitrators (e, f), voltammetric instruments (e), potentiostat (d–f), galvanostat (d), I/E converter (d), function generators (d, e), electrodes (a)	AMEL; Titristat
EG&G Princeton Applied Research	Potentiostat (d, e), coulometer (e), voltammetric instruments (d–f), function generators (e), electrodes, electrochemical HPLC detector (d), lock-in amplifiers (d–f)	
Environmental Science Associates	Voltammetric instruments, electrochemical HPLC detector	
Extech	*p*H meters, electrometers (a) conductivity meters (a), *p*H and other electrodes	*p*H simulator
Foxboro Analytical	Conductivity meters, *p*H meters, electrometers, *p*H and other electrodes	Process control; system engineering
Hach Chemical	*p*H meters, electrometers (a), conductivity meters (a), *p*H electrodes	Routine analysis
Harvard Apparatus	DO analyzer (c)	
HNU Systems	*p*H meters, electrometers (a–d), *p*H and other electrodes	
IBM Instruments	Voltammetric instruments (d–e), electrochemical HPLC detector (d)	
Ingold Electrodes	*p*H and other electrodes	
Ionics	*p*H meters, electrometers (g)	High-volume routine analytical systems
LG Nester	DO analyzer (b), *p*H meters, electrometers (a), *p*H electrodes	
Microelectrodes	*p*H electrodes	
Montedoro-Whitney	Conductivity meters (d), DO analyzer (c, d), *p*H meters, electrometers (d, e)	Multiparameter systems; long-term monitoring
Orion Research	*p*H meters, electrometers (a–d), conductivity meters (a), *p*H and other electrodes	
Petrolite Instruments	Potentiostat (g), voltage drop measurements (d)	Ac impedance bridge; corrosion measurements
Radiometer	Autotitrators (e–g), *p*H meters, electrometers (a–d)	
Rosemount (Uniloc)	*p*H meters, electrometers (a–d), conductivity meters (a, e), DO analyzer (a)	Process control
Sargent-Welch	Voltammetric instruments (d, e), *p*H meters, electrometers, conductivity meters	
Stonehart	Potentiostat	High performance
The Electrosynthesis Company	Coulometer (c), voltage drop measurements (b), electrodes	SU Electrosyncell for synthetic work
Wavetek	Function generators (d–f)	

*Includes *p*H, redox potential, and ion-selective electrode. †General price ranges in U.S. dollars: (a) ≤500, (b) 500 to 800, (c) 800 to 1200, (d) 1200 to 3300, (e) 3300 to 6000, (f) 600 to 12,000 (g) >12,000.

analytical mathematical solutions. Important mathematical techniques in routine use today include digital simulation (*16*) and numerical integration (*17*). In addition, powerful numerical methods are used routinely for analysis of experimental data (*18–20*). The work of Hanafey *et al.* (*21*) is an example of the power of these techniques and the extent to which they have been elaborated. But the use of a computer as a powerful calculator is quite different from its use as the heart of an electrochemical instrument.

Use of a small digital computer to control experiments and acquire and analyze data in electrochemistry was described by Lauer *et al.* in 1967 (*22*). Since that time the reliability of hardware has improved and its cost has dropped dramatically, and the flexibility and sophistication of software have increased as well. However, the principles on which today's computer-based systems are designed are the same. The major difference is that technical elaboration has made it possible to be a user with a smaller investment in knowledge of the system. That is, computer-based systems for electrochemistry have become more complex, and therefore can be treated more as black boxes. The general idea of increasing productivity by increasing the functional level at which a system needs to be understood was discussed recently by Enke *et al.* (*23*). The major problem with these systems is that they are not commercially available and are not readily adaptable from one laboratory to another. Brief exposure to one system quickly imparts the general principles of system design but does little to decrease the labor required to develop a similar but different system. As Dessy (*23a*) has pointed out, system development requires labor, talent, and money. For electrochemical applications distressingly large amounts of the first two of these scarce resources are required.

This situation is quite different from that in, for example, mass spectroscopy or nuclear magnetic resonance spectroscopy, for which a variety of companies offer systems incorporating powerful computers that in principle operate as black boxes. This difference arises partly from the difference in cost of the instrument controlled by the computer. In the case of mass spectroscopy, the hardware associated with the computer and interface is a small fraction of the total hardware cost, and that total cost easily supports the expensive software development required to turn the components into a system. In the case of electrochemical instrumentation, even in today's market, the opposite is true, and this has inhibited development of computer-based systems (*24*). Advances in very large-scale integration of electronic circuits and economies in producing read-only memories may change this situation. However, the forces driving these developments do not include the technical requirements of electrochemistry.

Faced with the perceived necessity of joining the computer age, many electrochemists have designed and built their own computer-based or microprocessor-based electrochemical systems (*25–28*). Faulkner (*28*) describes a modern version of the flexible instrument every electrochemist should want to have. The common experience of the experimenter is that of being set up to do one type of experiment, but obtaining a result which clearly requires that a different type of experiment be done to progress in understanding the system under study. Lack of good equipment for switching readily from one type of experiment to another is a major barrier to thorough scientific study of electrochemical problems. Analog hardware for handling this problem was described in 1963 by Lauer *et al.* (*29*). And the PAR 170, mentioned above, supplied in an analog framework much of the flexibility desired. The implementation of these ideas in a microprocessor-based instrument is a welcome development. However, this instrument is one of a kind; it has the merit of a demonstration project, not that of a commercial product.

More elaborate computer-based instruments involve such an investment in system development that ideally they should be designed to do experiments that would be otherwise impossible or impractical. Perhaps the best example is the work of D. E. Smith on fast-Fourier-transform a-c polarography. The computer-controlled system used for this work has been described (*30*); many applications and further refinements of the system have been published. In corrosion studies a-c impedance measurements are widely used, and the system of Smith and co-workers has been duplicated and used in this field (*31*). A second computer-based system for otherwise inaccessible experiments evolved directly from the original work of Lauer *et al.* (*22, 32*). The present system has been described briefly (*33*), and its use for square-wave voltammetry and other pulse techniques has been described for the general reader (*34*).

These systems provide power and flexibility for experimental control, data collection, and data analysis at the price of high development and overhead costs. The limiting factor is often availability of skilled workers. And necessarily the human investment in computer-based systems decreases the investment in electrochemistry. New techniques based on these capabilities cannot be reduced to practice for the general user without development of commercial instruments for their implementation.

Instruments for Measurement and Control

Sawyer and Roberts (*4*, chapter 5) have provided a short and well-balanced discussion of this topic which can serve as background material. Recent reviews by Stock (*35*), Johnson (*36*), Meyerhoff and Fraticell (*37*), and Kratochvil (*38*) provide useful surveys of the recent literature on electrochemical instruments (and a great deal else). Again, a distinction should be made between what is manifestly possible, as reported in the scientific literature, and what can be done in general practice—that is, what is commercially available. Because modern electrochemical instruments are complex, the average laboratory cannot construct and subsequently maintain them reliably and with ease. Here I will describe the present state of commercial instruments and suggest some directions the future might take.

Commercial instruments. Commercial instruments for electrochemistry may be grouped into several broad categories according to electrochemical function or application. Table 1 lists representative information on instruments designed to perform basic functions of measurement or control of potential, current, or charge and on equipment for analysis, monitoring, or process control (*39*).

Potentiometry is slighted in Table 1 because the measurement of potential in high-impedance circuits, once a demanding technical task, has now become routine, and modern instruments [*p*H meters, *p*Ion meters, and oxidation-reduction potential (ORP) meters] are of such high quality and modest cost that they rarely are a limiting factor in experimental work. It is the development of the electrodes (or sensors) themselves that limits applications. The technical and related commercial success of manufacturers in this area, notably Orion Research, is responsible for the dominant role of potentiometry in electroanalytical applications (*40*). Other successful technologies yield measurements of dissolved oxygen and of various forms of chlorine with membrane electrodes combined with amperometric measurements. The membrane provides a barrier through which gases diffuse and then react at the electrode surface, giving rise to a current proportional to the concentration of gas in the bulk solution. The membrane prevents other constituents of the solution from reaching the electrode and thus introduces selectivity and protects the electrode from fouling (*41*). The concept of using a membrane in these applications is related to fuel cell technology, and the method has been employed widely for determination of dissolved oxygen, as proposed by L. C. Clark (*42*). The use of membrane electrodes to determine free residual chlorine (Delta Scientific) is interesting, for the method combines simple theory with technology to produce a signal which is proportional to the concentration of hypochlorous acid, the effective disinfectant, and which does not respond to hypochlorite ion. The other very widespread electroanalytical method consists of the Karl Fischer and related amperometric titrations for determination of water (*43*). However, instrumental advances for water determination lie primarily in improvements in the mechanical properties of automatic burets rather than in improvements in control or measurement of electrical signals. The ECO Titristat provides a full range of potentiometric and amperometric titrations.

The most significant recent development in electroanalysis represented in Table 1 is that of electrochemical detectors for high-performance liquid chromatography (HPLC). Electrochemical detectors constitute about 5 percent of the HPLC detector market, and their unique properties of selectivity and sensitivity should enable them to maintain that share in the foreseeable future. Again, important developments are completely those of electrode design; the electronic aspects of present commercial detectors are routine.

Most of the equipment in Table 1 is designed for chemical analysis. Other application areas are electrosynthesis (The Electrosynthesis Company) and corrosion studies (Petrolite). Wavetek makes general-purpose laboratory electronic equipment that is useful in electrochemistry. Only EG&G Princeton Applied Research, ECO, and Astra Scientific International offer full lines of electrochemical equipment broadly useful in research and in a range of applications (synthesis, corrosion testing, analysis, battery testing, and so on). In general, this equipment is reliable, of good quality, and modest in price. EG&G Princeton Applied Research is the only company that makes and services its own equipment in the United States. It therefore has an advantage over ECO (vendors of AMEL instruments) and Astra (vendors of Tacussel instruments) with respect to compatibility and service. The latter is important, for these types of instruments, although seldom needing repair, are complex and tend to be impossible to repair without painstakingly accurate documentation.

Electrochemistry is more widely used now than it was 10 or even 5 years ago; this is reflected in the greater number and diversity of instruments available. New entries include those from Sargent-Welch, which, capitalizing on its trade name Polarograph, has reentered the market with a group of modular instruments built into a recorder and designed primarily for teaching, and IBM Instruments, which is apparently concentrating on analytical applications. But from the technical point of view the big news is no news; these instruments are mature in concept and in design.

Present Needs and Future Prospects

From the point of view of the analyst or the technologist, desirable improvements in electrochemical techniques are centered on general problems of sample handling and data treatment and on specific problems of cell design and electrode performance. Instrument performance specifically related to the nature of the electrochemical experiment (for instance, the rise time of a potentiostat) seldom limits the experiment. This generalization is also more or less true in electrochemical research. The intrinsic properties of the interface present a profound theoretical challenge as well as an instrumental one. While better instruments are always wished for (for instance, the elusive faster potentiostat), lack of good instruments does not seem to control our notions of the essence of the interface (*44*).

Electrochemical cells. Cell design, particularly since solutions must be deaerated in many cases, is and will remain a practical limitation. Improvements in cell design have been incremental; each "solution" of one aspect of the design problem has tended to exacerbate other aspects. We now have more rugged and more convenient cells than were used 10 years ago, but it seems that a new concept of how to carry out electrochemical experiments will be required to break through to a new level of practicality. As long as we are bound in our thinking by the traditional ways people have used their hands and eyes in the laboratory, we may be unable to imagine how to do things differently. In this context, developments in isotachophoresis may stimulate thought on how to carry out electrochemical experiments efficiently.

Electrodes. The other major problem area is the electrode. Electrode materials commonly in use today include mercury, many types of carbon, platinum, and gold, and, to a lesser extent, silver, tungsten, and nickel. These materials are used in all aspects of electrochemistry, including research, laboratory and commercial-scale electrolysis, and so on. Mercury electrodes are unique because they are liquid and therefore can provide a homogeneous and reproducible surface, especially in the mechanical design called the dropping mercury electrode (DME) (*45*). The mercury cells formerly in widespread use in the chlor-alkali industry gave the same good performance. A recent significant development in electrode design involving mercury is the EG&G Princeton Applied Research model 303 static mercury drop electrode. This electrode has a larger bore capillary than the DME, very high flow rates, and a plunger that seals the top of the capillary and controls drop size and rate of new drop formation. The plunger can be controlled automatically. This electrode is difficult to clean, fill, and maintain in a condition that ensures reproducible mercury drops; it also exhibits intermittent large resistance. However, when working properly it gives clean, stationary mercury drops at rates of about one per second and therefore makes possible experiments otherwise practically inaccessible. Apparently, other commercial instruments designed to provide the same function are now available. In addition, individual investigators have developed alternative designs (*46, 47*).

The reproducibility of mercury electrodes gives them a special role in fundamental studies of the properties of the interface and also in analytical application. But they are difficult to handle and have a limited positive potential range, and the mercury vapor and mercury-containing wastes present potential environmental hazards. Although it is easy to handle mercury safely, justifiable fears of its toxicity have led to reluctance to adopt procedures requiring use of mercury electrodes. It is not unreasonable to foresee routine use of mercury forbidden by law, and therefore it would be prudent to investigate vigorously substitute materials. In fact, most electrochemistry is now done with other types of electrodes.

The vagaries of all solid electrodes are the most important practical problem in carrying out electrochemical experiments. This is confirmed by the current popularity of research on "modified electrodes." A modified electrode is one that has been treated in a more-or-less determinate way to produce a surface with desirable and reproducible properties. The major practical success of this line of research, the dimensionally stable anode, was mentioned above. At present, the main impetus for research seems to be the search for electrocatalytic surfaces that will facilitate sluggish reactions. For example, consider the reaction overvoltage, 0.6 volt, for a modern Hall-Heroult cell for electrolysis of alumina. This overvoltage wastes about 1 percent of the electrical power generated in the United States. In principle, a catalytic modified anode surface could reduce the overvoltage to 0.1 volt or less. Modified electrodes would have applications in research, analysis, and battery design as well as in industrial electrolysis. And the most important applications, if this approach proves successful, will probably be those no one has thought of yet.

The problem of the performance of solid electrodes is also susceptible to attack by instrumental means. Computer-based systems are ideally suited for controlling the potential of an electrode by applying a series of potential steps, each of known duration. The values of the potential and the time interval between steps can be controlled precisely and can be selected arbitrarily under software control. For each electrode material and application, an appropriate potential-time function could be developed to optimize electrode performance. The present practice of "conditioning" solid electrodes provides a rudimentary suggestion of what might be achieved by this approach. However, the quantity and variety of research necessary cannot be done without widespread use of computer-based commercial equipment.

A further consideration is electrode size. Electrochemists are accustomed to seeing with normal vision the objects they are using. In some applications (corrosion testing, synthesis, and so on) electrodes are necessarily large, but in most research the electrode size is arbitrary. This has significant effects on instrument design. Large electrodes can require large currents, which create large voltage drops in solution and require high power for potential control, and that costs money. The AMEL potentiostat with 10-microsecond rise time that gives 1 ampere at 15 volts sells for $1072; the version supplying 10 amperes at 30 volts sells for $5600. Scaling down the size of experiments could radically decrease the cost and amounts of chemicals used and produce markets for such devices as disposable electrochemical sensors.

Conclusions

Electrochemical instrumentation is now in a state of mature development. Electrochemists involved in research tend to design and build their own instrument systems as needed in addition to using commercial instruments. But the translation of research results into useful applications requires commercial instruments. Because the vitality of research depends ultimately on the practical importance of its applications (*48*), appropriate commercial instruments must be developed to sustain progress. Coupling of the components of this cycle appears to be stochastic, making it difficult to predict future developments. Microprocessors are routinely employed in applications-oriented electrochemical instruments, but their purpose is mainly to handle data; they are peripheral to the electrochemical experiment. Computers are essential for many types of research in electrochemistry, both for computation and for experiment control and data acquisition. However, developments in computer-based instruments will depend on other markets for computers rather than on the requirements of electrochemical research.

References and Notes

1. H. A. Laitinen and G. W. Ewing, Eds., *A History of Analytical Chemistry* (Division of Analytical Chemistry, American Chemical Society, Washington, D.C., 1977).
2. An interesting discussion of the development of this instrument is contained in (*1*), pp. 275–279.
3. J. B. Flato, *Anal. Chem.* **44**, 75A (1972).
4. D. T. Sawyer and J. L. Roberts, Jr., *Experimental Electrochemistry for Chemists* (Wiley, New York, 1974).
5. A. L. Hodgkin, A. F. Huxley, B. Katz, *J. Physiol. (London)* **116**, 424 (1952).
6. At the Gordon Research Conference in Electrochemistry the flow patterns of information confirm the confidentiality of significant industrial research, but also suggest that current developments in electrochemical research and instrumentation might be practically significant.
7. An exception to this generalization is the use of impedance techniques to study corrosion of metal surfaces, which is discussed further later in this article.
8. J. O'M. Bockris, B. E. Conway, E. Yeager, R. E. White, Eds., *Comprehensive Treatise of Electrochemistry* (Plenum, New York, 1981).
9. An entertaining historical view is presented by W. M. Clark, *Oxidation-Reduction Potentials of Organic Systems* (Williams & Wilkins, Baltimore, 1960), chapter 1.
10. P. Delahay, *Double Layer and Electrode Kinetics* (Wiley-Interscience, New York, 1965).
11. C. A. Barlow, Jr., and J. R. MacDonald, *Adv. Electrochem. Electrochem. Eng.* **6**, 1 (1967).
12. R. Tamamushi, *Kinetic Parameters of Electrode Reactions of Metallic Compounds* (Butterworths, London, 1975).
13. L. Meites and P. Zuman, Eds., *Handbook Series in Organic Electrochemistry* (CRC Press, Boca Raton, Fla.).
14. J. J. Auborn, K. W. French, S. I. Lieberman, V. K. Shah, A. Heller, *J. Electrochem. Soc.* **120**, 1613 (1973).
15. C. G. Enke, *Science* **215**, 785 (1982).
16. D. Britz, *Digital Simulation in Electrochemistry*, vol. 23 of *Lecture Notes in Chemistry*, G. Berthier *et al.*, Eds. (Springer-Verlag, New York, 1981).
17. R. S. Nicholson and M. L. Olmstead, in *Computers in Chemistry and Instrumentation*, vol. 2, *Electrochemistry: Calculations, Simulation and Instrumentation*, J. S. Mattson, H. B. Mark, H. C. MacDonald, Eds. (Dekker, New York, 1972), pp. 118–197.
18. S. N. Deming and S. N. Morgan, *Anal. Chem.* **45**, 278A (1973).
19. A. Savitzky and M. J. E. Golay, *ibid.* **36**, 1627 (1964).
20. R. A. DePalma and S. P. Perone, *ibid.* **51**, 829 (1979).
21. M. K. Hanafey, R. L. Scott, T. H. Ridgway, C. N. Reilley, *ibid.* **50**, 116 (1978).
22. G. Lauer, R. Abel, F. C. Anson, *ibid.* **39**, 765 (1967).
23. C. G. Enke *et al.*, *ibid.* **54**, 367A (1982).

23a. R. Dessy, *J. Chem. Ed.* **59**, 321 (1982).

24. Marketing also plays a role. It is widely believed that while other advanced computer-based instruments such as the Fourier-transform infrared interferometer have unique capabilities that create new markets, in electrochemistry modern instruments would just displace sales for existing models.
25. J. A. Harrison and C. E. Small, *Electrochim. Acta* **25**, 447 (1980).
26. J. F. Price, S. L. Cooke, Jr., R. P. Baldwin, *Anal. Chem.* **54**, 1011 (1982).
27. J. E. Anderson and A. M. Bond, *ibid.* **53**, 1394 (1981).
28. P. He, J. P. Avery, L. R. Faulkner, *ibid.* **54**, 131A (1982).
29. G. Lauer, H. Schlein, R. A. Osteryoung, *ibid.* **35**, 1789 (1963).
30. R. J. Schwall, A. M. Bond, R. J. Lloyd, J. G. Larsen, D. E. Smith, *ibid.* **49**, 1797 (1977).
31. W. H. Smyrl, in *Electrochemical Corrosion Testing*, F. Mansfeld and U. Bertocci, Eds. (ASTM STP 727, American Society for Testing and Materials, Philadelphia, 1981), pp. 198–214.
32. G. Lauer and R. A. Osteryoung, *Anal. Chem.* **40**, 30A (1968).
33. T. R. Brumleve, J. J. O'Dea, R. A. Osteryoung, J. Osteryoung, *ibid.* **53**, 702 (1981).
34. S. A. Borman, *ibid.* **54**, 698A (1982).
35. J. T. Stock, *ibid.*, p. 1R.
36. D. C. Johnson, *ibid.*, p. 9R.
37. M. E. Meyerhoff and Y. M. Fraticelli, *ibid.*, p. 27R.
38. B. Kratochvil, *ibid.*, p. 105R.
39. Information for Table 1 was obtained by request to all companies listed in (i) the AAAS *Guide to Scientific Instruments* (1980–1981) and (ii) the American Chemical Society's *Analytical Chemistry Lab Guide* (1981–1982) under the subject headings (i) electrochemical cells, dropping mercury electrode assemblies, solid polarographic (sic) electrodes, specific ion electrodes, polarographic analyzers, potentiostats, and wave form generators, and (ii) coulometers, dropping mercury electrodes, glassy carbon electrodes, graphite electrodes, metallic electrodes, wave form generators for electrochemistry, polarographic equipment and accessories, and potentiostats. Because of the very large number of manufacturers and venders of *p*H electrodes, this category was not included. I sent 72 requests and received 34 replies.
40. D. Midgley and K. Torrance, *Potentiometric Water Analysis* (Wiley, New York, 1978); see especially chapter 7.
41. Fouling refers collectively to processes such as adsorption which degrade electrode performance; it is the limiting factor in most electrochemical applications for process control, monitoring, or high-volume analysis.
42. M. L. Hitchman, *Measurement of Dissolved Oxygen* (Wiley, New York, 1978).
43. J. Mitchell, Jr., and D. M. Smith, *Aquametry* (Wiley, New York, ed. 2, in press), part II.
44. Of course, instruments are the eyes we use to view the interface, and better vision might dramatically alter our perception. This is the basis for the widespread use of spectroscopy to study electrochemical problems, a subject beyond the scope of this article.
45. The DME consists of a piece of glass capillary tubing (inner diameter, ~ 50 micrometers) through which mercury is forced under constant head at a flow rate of about 1 milligram per second. The drops of mercury that grow and fall off the end of the capillary at the rate of about one per 5 seconds constitute the electrode. J. Herovsky was awarded the Nobel Prize in Chemistry in 1959 for his serendipitous discovery of the usefulness of this device.
46. W. A. Byers and S. P. Perone, in preparation.
47. L. Gierst and co-workers have discussed a device based on the DME with vacuum compensation of the head of mercury to provide a stationary drop of arbitrary size.
48. This point was elaborated on by N. Hackerman, *Chem. Eng. News* **60**, 30 (9 August 1982).

49. I thank R. A. Osteryoung for helpful comments. Preparation of this article was supported in part by NSF grant CHE7917542.