

Some Observations on Conducting Research in the Digital Era

by Eliezer Gileadi

This is obviously a very happy day in my life, and one of the most important days in my scientific career. It is important therefore to put things in perspective, and a measure of humility is called for. I would like to start by thanking the Honors & Awards Committee for choosing me to be the recipient of the Olin Palladium Award for the year 2003. Whatever scientific achievements I may have had to justify their decision, it also indicates, I am happy to say, that over the past 40 years as an electrochemist I must have made many more friends than enemies!

When it comes to a highly coveted award like this, the choice is not easy. Whoever the other candidates might have been, I am sure that some of them were worthy candidates, and I would like to wish them success the next time they are nominated.

I would like to acknowledge my parents. I am what you might call "a first generation academic." My parents had only a high school education, and not a very good one at that, but their desire for knowledge and their curiosity were insatiable. The Jews like to refer to themselves as "The Nation of the Book." This is probably in reference of "The Book," namely The Bible, or more precisely, The Old Testament, which we call in Hebrew the Tanach, but the Jewish culture and tradition of learning extend far beyond that. When I was a teenager, the usual pastime in the evening was reading. After supper we would sit, my late parents and sister and I, around the table for a couple of hours, each reading a book. Once in a while, when one of us would come across an interesting piece of information, a piece of humor, a particularly beautiful linguistic expression or any subject of some general importance, we would discuss it for a while, and then plunge back each to his or her book.

The dedication in my textbook on Electrode Kinetics, published in 1993 is, "Dedicated to my parents, who valued the book above all treasures of the human race." This was not meant to be a poetic statement – it is the bare and simple truth.

The tradition of reading has not been lost. Both my wife and I are avid readers. So are all our five children and out of our nine grandchildren, the four older ones, who are already teenagers, are also addicted to reading books. We often complain about the shortcom-

ings of the educational system, and often we are right. But just as it is often said that charity starts at home, it should also be remembered that education starts at home as well.

Next I would like to thank my wife Dalia, who is here in the audience today, of course. Her understanding, encouragement, dedication and above all her love helped me to be what I am today. Without her I would not be here today to receive this prestigious award.

The person who showed me the beauty of science was the late Prof. Aharon Katchalsky-Katzir. I took my first physical chemistry course with him. Early on he started teaching us the laws of diffusion. Why is it that thermal motion, which is obviously random, always drives molecules down the concentration gradient? How could the random thermal motion of molecules have a vector associated with it? The answer is obvious now, but then, at a young age, just out of high school, it was not. Having explained the physics behind the diffusion process, he wrote Fick's first law on the board, namely

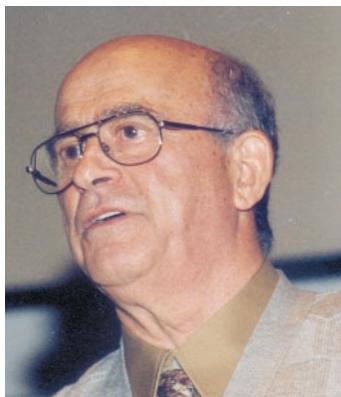
$$flux = -D(\partial C / \partial x) \quad [1]$$

We, the students, were all happy with that, but then came the surprise: "But this equation is wrong," he said. And he challenged us to find out what was wrong with it! This was more than fifty years ago, and as far as I can remember, none of us came up with the right answer. It is wrong, he said eventually,

when we all gave up, because we made the tacit assumption that the diffusion coefficient itself was independent of concentration. This may be a very good approximation in many cases, but it is never rigorously true! What we have learned there, which I have been trying to pass on to my students as a motto in the study of science is "Never forget the ubiquitous tacit assumption." What we learned, in addition to some facts in physical chemistry, was to be always alert and critical. To be wary of complex

mathematics: it may look very impressive, but is the model used acceptable? Prof. Aharon Katchalsky-Katzir was a great teacher, and I owe him much of my critical approach to science, as well as my dedication to it. His life ended at a relatively young age in

The 2003 Olin Palladium Award was presented to Eliezer Gileadi in recognition of distinguished contributions to the field of electrochemical or corrosion science. The award recognizes outstanding contributions to the fundamental understanding of all types of electrochemical and corrosion phenomena and processes. Dr. Gileadi of Tel-Aviv University, Israel, was presented with the award at the 204th Meeting of the Society in Orlando, Florida, on October 13, 2003. The text of his address is published here.



a dismal way – he was gunned down at Tel Aviv Airport, together with a dozen other innocent people, by a terrorist.

Next I would like to thank my former mentor and present friend, Prof. Brian E. Conway, for the wonderful three years I spent with him doing my PhD and a short postdoctoral fellowship. From Brian I learned how science really works. The joy of scientific discussion was at its peak – just science for the sake of science, no one-upmanship, not even the slightest implication of authority, just an earnest and sincere attempt to solve the next scientific problem.

Among my colleagues I would like to mention first Emilia Kirowa-Eisner, with whom I have collaborated for the past 35 years. We have written many papers together and had numerous wonderful discussions. We have learned a lot from each other, and I can only hope that this collaboration will continue for a long time to come.

My collaboration with Glenn Stoner dates back to 1964, when he arrived as a graduate student in Philadelphia, and continued after he moved to UVA. The hospitality and friendship extended to me by Glenn, his wife Marlene, and their three boys during my numerous visits to Charlottesville made that city my second hometown. This also gave me the opportunity to meet many of his graduate students, with some of whom I had the pleasure of scientific collaboration over the years.

At the University of Pennsylvania I also met Srinivasan Subramanian, called Srimi for short, who has been my good friend ever since. He was our local mathematical wizard. When there was an equation to solve Srimi would look at it, think a minute, and write down the solution. We overlapped for nearly three years, learned a lot from each other, wrote a few papers together, and consoled each other when the going got rough.

Later I had close collaboration with Emanuel Peled in the field of non-aqueous electrochemistry; until he became a faculty member and struck out on his own, to become a first class expert in non-aqueous batteries and electrochemical energy conversion.

In 1991 I was very lucky to have Vladimir Tsionsky, formerly from the Frumkin Institute of Electrochemistry in Moscow, join my group in Tel-Aviv. One of the wonderful aspects of being a scientist is that we often know and learn to appreciate each other by reading each other's papers, long before an opportunity to meet in person presents itself. So, when Vladimir first showed up in my office, it felt like we have been friends for years. Since he arrived, our friendship has grown and intensified, and the scientific collaboration between us has been wonderful.

Finally I would like to mention my good friend Barry MacDougall, with whom I have been collaborating scientifically during the past ten years, during recurring visits in his laboratory at the NRC in Ottawa. As some of you may know, Barry did his PhD also with Brian Conway, assisted by Halina Kozłowska, and must have had experiences similar to mine. The long and profound discussions we have been having every summer for the past ten years remind me of the discussions I used to have with Brian – all intellectual pleasure.

Some General Issues in Science

The rapid growth of science and technology—I belong to a lucky generation that has seen an immense revolution in our understanding of science and the resulting changes in technology within one lifetime. Changes have been certainly more profound than ever before and it may be a long time before another generation will be exposed to similar changes in such a short span of time. Allow me to mention just a few random examples, by no means a comprehensive list, for the benefit of the younger generation in the audience.

- Haber developed a method for the fixation of nitrogen in 1922. This opened the way for manufacturing of chemical fertilizer, which revolutionized farming and increased food supplies.
- Fermi, the Italian genius of physics, performed the first transmutation of elements in 1932, and the first nuclear reactor came on line in about 1943.
- Penicillin was discovered in 1942, followed by the whole field of antibiotics.
- The physics of semiconductors, upon which transistors and later the whole field of microelectronics is based, was developed in 1948.
- The laser was invented in the early sixties. It had been realized immediately that this device could eventually be important, but people did not quite know for what. It was initially referred to as “a solution looking for a problem.”
- Hand-held calculators first became available in the early seventies. Before that we used logarithmic tables, (and some of us just used their brains, which was a rather common practice in those primitive days gone by), to do complex calculations. In 1964 I purchased the first electronic calculator for the group at the University of Pennsylvania. It could only do the four basic arithmetic operations, was the size of a large typewriter and cost \$2,000, which is roughly equivalent to about \$10,000 today. The rest, as they say, is history.
- Personal computers first appeared only in the mid-seventies, and did not become part of almost every household until the beginning of the nineties.

One could go on and on, but the point I want to make is the following. Some of these developments led to what can be regarded, in my opinion, as the digital revolution, which changed the way experiments are performed and indeed our whole attitude toward scientific research.

The digital revolution in scientific measurements—Before the Digital Revolution (BDR), our main effort was centered on making accurate measurements. Reading the current or the potential on a meter was limited by the linearity of the scale and by our ability to read the result accurately. Some instruments were equipped with a mirror behind the scale to prevent parallax. To make a real accurate measurement one used a bridge, in which resistors and capacitor were balanced to obtain a zero reading. In short, our ability to understand the physical world around us and formulate the laws by which it operates was limited by our ability to measure it accurately enough.

Now, After the Digital Revolution (ADR), we can measure everything with superb accuracy. But can we understand the data? In electrochemistry, for example, it is easy to measure the potential with respect to a reference electrode with an accuracy of $\pm 1 \mu\text{V}$, but in most cases we cannot reproduce the chemistry to better than $\pm 1 \text{ mV}$.

The above comments do not imply that the digital revolution is bad for science – it is indeed wonderful. It allows us to concentrate our attention on understanding nature, not on barely trying to measure it. But since we can measure more accurately, we observe a lot more of the fine structure of physical phenomena, and great care in interpreting the data is called for.

Adding My Name to the Guinness Book of Records

Recently a colleague presented his work in our electrochemistry seminar. He was asked about the sensitivity of his measurement – could he do it at a lower concentration? I loved his

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answer. He said, "It has not been my intention to enter the Guinness Book of Records. I just wanted to understand what was going on." I loved it, because too many of us do just that, measure something with the highest sensitivity, the fastest transient, the smallest number of molecules etc., to achieve a new record, to be included in the Guinness Book of Records. What was the question? What is the new insight gained? Who cares, as long as you were the first ever to have made such a wonderful measurement?

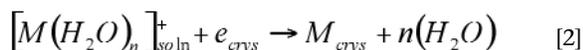
There is nothing wrong in making more accurate measurements. It is one of the most important endeavors in science. It may be a problem, however, if it becomes the only route taken, or even if it becomes our most important endeavor. We must raise our heads once in a while from the bench and look over the horizon. After all, measurements are just one of the tools we use to understand science; they have no inherent value of their own.

It is somewhat unfortunate that the current generation of successful scientist have mostly become a generation of equipment builders rather than of deep thinkers. But that is where the glory is. That is where chasing the citation index has been driving us all. That is where the digital revolution has taken most of us. Even theoreticians tend to follow a similar trend. They too find it expedient to jump from one field to another, whichever happens to be the most fashionable at the moment, instead of persisting in solving deep problems. It is likely to lead to more citations, more invited lectures, more paper – and consequently faster promotions. How wonderful would it be if we could bar the use of statistical data in the deliberations of promotion and tenure committees?

Next thing we know, each candidate for promotion or tenure will be represented by a lawyer in the appropriate committee – that would surely be the end of excellence at universities, as we know it!

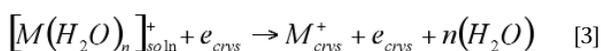
Highlights of Our Recent Work

Electron transfer during metal deposition and dissolution—For a long time I have been fascinated with the apparently simple process of metal deposition. It is written in the form



The energies of hydration have been calculated. For monovalent ions they are about 5 eV and they increase sharply with charge. Thus, metal ions are strongly stabilized by hydration, and they have to shed this hydration shell in order to be incorporated into the metal lattice. One might tentatively expect that metal deposition would be a very slow process, but the opposite is observed experimentally. The rate constants for deposition of some of the metals are the highest among electrode reactions known.

I consider this to be one of the open questions in electrode kinetics, which has been ignored in the literature. But there is more to it than that! Equation 2 cannot be the correct representation of the metal deposition process, since it implies that metals consist of neutral atoms, while it is well known that they consist of a lattice of positive ions immersed in a cloud of delocalized electrons. Accordingly, Eq. 2 should be rewritten as



This apparently formal change in the way the equation is written makes a great difference in the model that should be

10 mV/sec -4.8C
0.1 M HClO₄

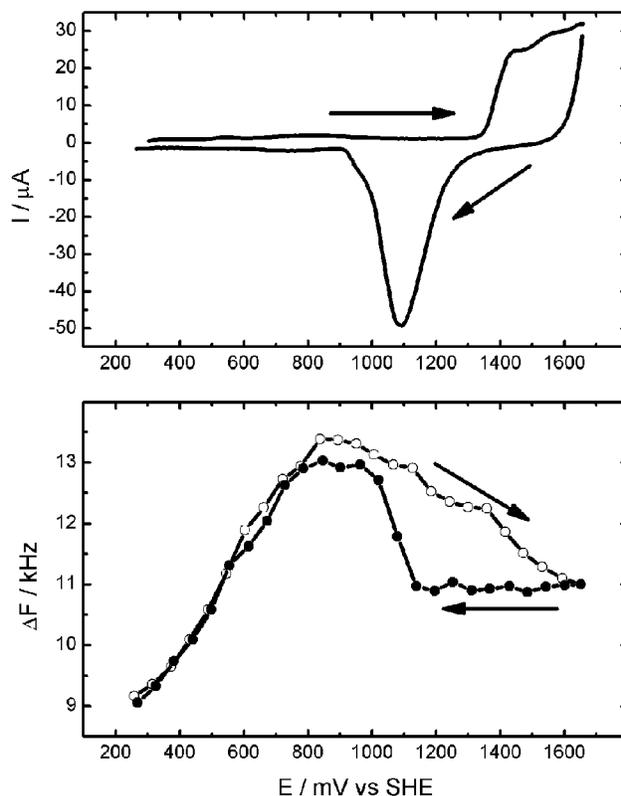
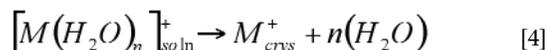


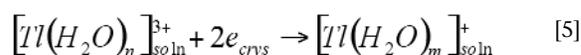
Fig. 1. The resonance frequency of a gold-coated EQCM in contact with a LLL (0.1M HClO₄) at -4.8°C, as a function of potential. The corresponding cyclic voltammetry (10mV/s) scan is shown above.^{1,2}

used to discuss the kinetics of this process. What it shows is that the electrons were in the crystal lattice in the initial state, and they are there in the final state. Indeed the overall reaction of metal deposition should be written as



All we have done in the transition from Eq. 3 to Eq. 4 was to eliminate species that appear on both sides of the equation, which is how we learn to balance chemical equations in the freshman chemistry course. But the consequence is far reaching. Because electrons do not take part in the overall reaction, there is no reason to assume that they would participate in the transfer of charge across the interface! Indeed, there is every reason to believe that they would not. The same argument can also be made for metal dissolution.

If we accept the above argument, we have to rethink the whole field of metal deposition and dissolution. The theory of charge transfer in electrode kinetics has been, in essence, synonymous with the theory of electron transfer. Admittedly, ion transfer has been discussed as a partial alternative, but only as a partial one. In such theories the ion is assumed to penetrate the double layer to some extent, but deposition of the metal ion is not considered to be over until an electron has been transferred across the interface. This may no longer be the correct model to use. This does not apply to redox reactions such as



where electrons are exchanged between the metal and some species in solution. In Eq. 5, two electrons, which were in the crystal in the initial state, end up as part on the monovalent Ti^+ ion in the final state. Similarly during hydrogen evolution, the electrons transferred from the metal to H_3O^+ ions would be carried away in the H_2 molecules to the gas phase. This is qualitatively different from the case shown by Eq. 3 and 4.

Liquid-like Layers (LLL)—The first to observe the phenomenon of surface-pre-melting, leading to the formation of a liquid-like layer at the surface of ice was Faraday. The phenomenon is important in determining natural phenomena such as the sliding of glaciers and the generation of hailstorms, for engineering problems such as the frosting of aircraft wings and formation of ice on high-power transmission lines, as well as for our fundamental understanding of the structure of interfaces. Electrochemistry provides a special opportunity to study this phenomenon, because the surface can be modified *in situ* by controlling the potential across a metal/frozen electrolyte interface, and by modifying the surface of the metal. Employing an EQCM and studying its admittance spectrum allowed us to develop models describing the properties of the LLL under different experimental conditions.^{1,2}

In Fig. 1 we show the resonance frequency as a function of potential for a LLL formed at the surface of a frozen electrolyte, consisting of a 0.1 M solution of HClO_4 , in contact with a gold surface at -4.8°C . It is noted that the frequency changes with potential by as much as 4 kHz in the double-layer region, where the nature of the surface of gold is believed to be independent of potential. This change is independent of the direction of the potential sweep.

The behavior at 1.3 V (SHE) is of particular interest. When this potential is reached in the anodic sweep, the surface is bare, while when it is reached in the cathodic sweep, the surface is covered with a monolayer of oxide, as seen from the cyclic voltammogram. The resonance frequency differs by about 1.5 kHz on the two surfaces, even though the potential is the same. While these results are still preliminary, they clearly show the opportunities and challenges offered by employing this additional tool for the study of the properties of liquid-like layers in the context of interfacial electrochemistry.

Simultaneous 2-e transfer—Since I entered the field of electrochemistry, more than 40 years ago, it seemed to have been generally accepted that electrons were transferred one at a time. Could two electrons be transferred simultaneously? The common wisdom said categorically NO. I have never actually seen a proof of this assertion, but it was stated in all textbooks (including, alas, two of my own!) in an axiomatic manner. When discussing the matter with colleagues, it was tentatively argued that (1) electrons were transferred across the interface by tunneling; (2) the probability of tunneling was very low; and (3) the probability of simultaneous tunneling of two electrons (assuming these were independent random events) would therefore be negligible.

The need to assume that electrons must be transferred one at a time had a significant impact on the interpretation of the mechanism of electrode reactions. For divalent ions such as Fe^{2+} or Ni^{2+} to follow this path, one would have to assume that a monovalent intermediate was formed. Such species are not known to exist in aqueous solution. It could be argued that the intermediate is stabilized by chemisorption on the surface, but the experimental evidence for the existence of such adsorbed species is mostly lacking.

This issue becomes irrelevant in the framework of the model proposed above for metal deposition and dissolution. If elec-

trons do not participate in charge transfer, then the need to assume the existence of unstable intermediates becomes redundant. The question is still relevant, however, for the other class of electrode reactions, such as that given in Eq. 5.

It would seem obvious that there must be an upper limit to the instability of the assumed intermediate, beyond which simultaneous 2-e transfer would be the faster pathway. Finding this limit was the problem I set out to solve. The theory of Marcus was used for this purpose, and only the main results are given here.

The standard Gibbs energy of activation is given by the expression

$$\Delta G_1^{0\#} = \frac{(\lambda_1 + \Delta G_1^0)^2}{4\lambda_1} \quad [6]$$

where λ , ΔG^0 and $\Delta G^{0\#}$ are the solvent reorganization energy, the standard Gibbs energy of formation of the product and the standard Gibbs energy of activation for the formation of the product, respectively. The subscript represents the number of electrons transferred. The solvent reorganization energy is sensitive to the amount of charge transferred. For the transfer of z electrons it is given approximately by

$$\lambda_z = z^2 \times \lambda_1 \quad [7]$$

Combining the last two equations we find that the equation which satisfies the equality

$$\Delta G_1^{0\#} = \Delta G_2^{0\#} \quad [8]$$

is

$$\Delta G_1^0 = \lambda_1 + \Delta G_2^0 / 2 \quad [9]$$

All the points on the plot of ΔG_1^0 vs. λ_1 satisfy Eq. 9. A detailed discussion of this problem is given in a recent publication.³

The important conclusion is that, using commonly accepted values for the solvent reorganization energy, a moderate level of instability of the intermediate would make the simultaneous 2-e transfer the faster and hence the more likely pathway. This treatment ignores the pre-exponential factor in the rate equation. However, since the rate of reaction is proportional to the exponent of the standard Gibbs energy of activation, this is expected to be the predominant factor determining the pathway followed. ■

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About the Author

ELIEZER GILEADI is Professor Emeritus of Chemistry, in the School of Chemistry, at Tel-Aviv University, Tel-Aviv, Israel.