

A VOLUME IN HONOR OF J. O'M. BOCKRIS

ELECTROCHEMISTRY

The Past Thirty and the Next Thirty Years

Edited by

Harry Bloom and Felix Gutmann

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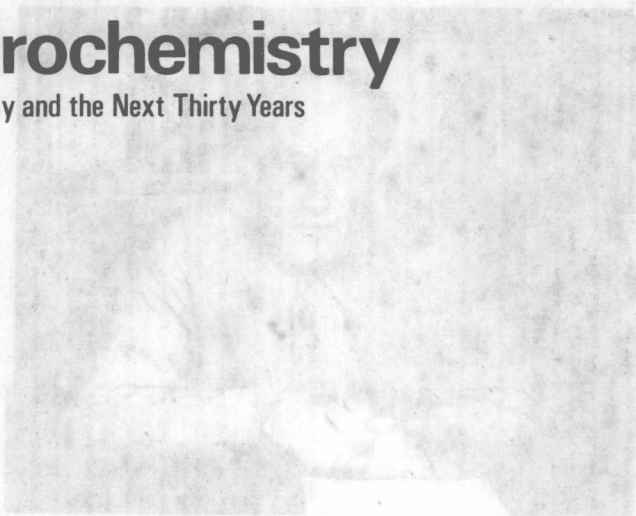
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Electrochemistry

The Past Thirty and the Next Thirty Years



J. O'M. Bockris



J. O'M. Bockris

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Preface

Some time ago a group of present and former collaborators of Professor John O'M. Bockris, following a suggestion by Professor J. D. Mackenzie (Los Angeles), conceived the idea of an International Symposium devoted to reviewing the active and developing aspects of the science of electrochemistry. From this beginning has sprung the "Electrochemistry Symposium—The Past Thirty and the Next Thirty Years," which took place at Imperial College, London, from April 3-6, 1975.

The plan for this symposium is unusual, since it features pairs of invited addresses, one to summarize the "state of the art" and the other to suggest directions for future research in particular aspects of electrochemistry.

This volume of proceedings gives these papers in their final, considered, and fully referenced form, arranged in the sequence of their delivery at the symposium. Also included are introductory addresses given by Professor Ubbelohde, Professor Frumkin, Dr. Egan, and Dr. Inman.

Both aspects of nearly every topic, plus the discussions, are integrated in a Report or Summary. A synopsis of the matters raised at the symposium and prepared by Professor John O'M. Bockris closes this volume.

The cooperation of Plenum Press, New York, is gratefully acknowledged.

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Introductory Address

A. R. Ubbelohde

A provocative list of electrochemical themes has been prepared, and their discussion is likely to yield new inspiration in science and engineering, in more than one direction.

It is the privilege of the person opening the symposium to select those parts of the program for comment which appeal to him particularly, without having to confess ignorance about some of the other themes on the bill of fare. I don't want to take up this privilege, so I will start with some of my favorites, but will then go on to humble confessions.

Quite definitely, electro-organic chemistry is my favorite. I consider that the physical chemistry and in particular the bond-reaction chemistry of organic ions to be pregnant with all kinds of unexplored innovations. When an organic ion is discharged at an electrode, we all know the rather elementary formulation of Kolbe reactions leading mainly to radical pairing. But in fact, electrode discharge is one of the most versatile means for producing an enormous variety of organic free radicals. The behavior of these radicals immediately before or immediately after the ion is discharged at an electrode must in principle permit various kinds of bond rearrangements, if the molecular structure is at all complex. Furthermore, although the electrode material imposes a constraint on the course of the reactions, one should be able to present other reaction alternatives to the free radical, which may prefer these to Kolbe pairing with a neighbor. For example, it should be interesting to "flood" an electrode with a gas capable of reacting with free radicals, such as ethylene, acetylene, oxygen, or a halogen. This could become a route to reaction products quite different from the usual Kolbe-paired radicals.

Quite possibly, some of the more interesting possibilities can only be realized at elevated temperatures, above the boiling point of electrolytes in conventional solutions. In this sense, developments of organic electrolysis in molten salts, particularly organic salts of low melting point such as the groups of substances we have recently been studying in my laboratories, considerably extend as well as raise the range of working temperatures available.

I should add that in addition to yielding a diversity of organic products after bond rearrangement, some free radicals produced by the discharge of organic cations will amalgamate with mercury, forming the so-called "ammonium amalgams" in which they dissolve and are stabilized after losing an electron by transfer to the electron band of the liquid metal.

These fascinating avenues for further inquiry depend in part on technological innovations in the study of what happens at an electrode, i.e., of *electrode processes*. Our ignorance about the detailed physical chemistry of electrode processes is partly due to our comparative ignorance of solid-state reaction chemistry. The surface of most conventional electrodes is (geometrically) very restricted, which means that only those reactions can be conveniently studied for which the electrode surface is "self-clearing." Quite possibly use of fluidized-bed electrodes, or dispersed liquid electrodes, will offer much more favor-

able conditions for investigating and indeed for using novel electrode processes on the large scale.

This brings me back to two other principal themes due to be discussed near the beginning of this symposium. The subject of electrocatalysis is full of intriguing possibilities since: (1) The electrode surface can be continually renewed by exchange with the electrolyte. (2) More than a single reactive molecular species can be brought up to the electrode/electrolyte interface during electrolysis. The activating regime prevailing there during electrolysis may well catalyze chemical reactions between molecules impinging on it, because of its "freshness," being kept free from poisons as it were.

Some years ago I invented a special case of "electrocatalysis" in which catalytic reactions were studied at the back of a thin septum electrode during active electrolysis on its other face. "Septum hydrogenation," which was the principal reaction I studied, did show certain interesting possibilities. Again these might be more rewarding at higher temperatures, with molten salt electrolytes, than with the aqueous electrolytes I used.

Electrode processes in relation to solid-state reactions are in my view also very much wrapped up with electrochemical problems of *energy conversion*, at any rate from the particular aspect of storage of electrical energy in a secondary cell. Presumably, the reason the lead accumulator has had such a long and successful history is because the solid-state reactions at the electrolyte/electrode interface can occur in both charge and discharge directions, with little or no irreversible hindrances. But the heavy weight per unit charge of this secondary cell militates greatly against its wider uses. There *must* be other electrode/electrolyte interface reactions less objectionable from this point of view; quite possibly, working at somewhat higher temperatures using molten salts will offer possibilities of secondary cells not available with solutions of electrolytes.

Obviously, like every physical chemist who has done research on cooperative hydrogen bonds in solids, I am tempted to stick my neck out concerning *bioelectrochemistry*. But perhaps I had better not venture too far except to wish well for the discussion of this very provocative theme.

I also note with pleasure substantial themes of longstanding importance, such as corrosion, electrowinning of aluminum and of other metals, and mineral processing. I may just mention the very recent founding of a new Kodak Chair of Interface Science at Imperial College in my department. All kinds of electrochemical problems are basically interface problems, and we can confidently have hope for progress in this direction too for the years ahead.

Finally, in wishing well for the days of discussion ahead you may desire an electrochemical comment even about the symposium dinner. Unfortunately I cannot be present at this so I will publish my contribution beforehand. I may term it the Ubbelohde electrochemical couple, measured by our lips when we are drinking wine or beer. If you think of it, when you bring a glass to your lips you cannot help forming an electrochemical couple; indeed, wine or beer tastes quite different from cups of conducting materials such as gold, silver, and pewter compared with nonconductors such as glass or porcelain. My theory requires that the electrochemical couple is different in each case. Note that I will not classify milk or tea as electrolytes—although perhaps I must compromise over Coca-Cola!

Chairman's Opening Remarks

Douglas Inman

On a practical note, let me first welcome you to Imperial College, and apologize for the organizational difficulties which during the last few months have made your successful arrival here as difficult as possible!

I wish to say very little at this stage as, certainly, at least with regard to electrochemical science, it is all going to be said during the course of our proceedings. The second report to the Club of Rome, which has just appeared, is entitled: "Mankind at the Turning Point," and it is of course our contention that electrochemical science will make a major and necessary contribution to man's existence on earth in the years which lie ahead. Although electrochemists are often more concerned with interphases rather than interfaces, the year 1975 is a well-defined landmark of the second type as it is now 30 years after the finish of World War II and the year in which Professor Bockris obtained his Ph.D., whereas 30 years from now we shall be 5 years into the much-heralded 21st century.

I can distinguish four main levels of technology. These are the perhaps illusory, blissful state of no technology, the state of labor-intensive intermediate technology which is perhaps most suitable for some of the undeveloped regions of the world, the state of Western technology from the early 20th century to the present day which we should be busily exporting to the underdeveloped nations to allow them to expand economically, and advanced technology which will be necessary in the looped spaceship Earth economy which the developed nations will have to pursue if they and indeed the rest of the world are to survive. This advanced technology, which will necessarily have to concentrate less on throughput and more on a materials- and energy-conserving and pollution-minimizing economy, will without doubt contain a large contribution of the electrochemical science which we are to discuss during the next four days.

