

Part F

EPILOGUE

CHAPTER 17

Moving Frontiers in Electrochemistry

- 17.1 Introduction
- 17.2 The models and methods
- 17.3 Solution phase processes
- 17.4 Surface processes
- 17.5 Catalysis and inhibition
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- 17.7 Towards the future

17.1 INTRODUCTION

In the preceding pages, we have taken a complete trip around the garden of electrochemical knowledge, covering many paths leading to the emerging frontiers in the garden. Due to many obvious limitations, we have not tried to see each region quite comprehensively. But we have certainly tried to obtain an overview, the themes, the concepts and the specialities of different regions that are growing around the centre. With this type of a general purpose trip, we hope that our readers can move in the path they choose and walk along with confidence towards the frontiers of knowledge in their own specialization. What is even more interesting is that they would find that the frontiers they have chosen to specialize are themselves moving ahead at a faster pace.

Interesting as it may be, the arrangements for the trip to electrochemical frontiers through cyclic voltammetry was quite a challenging task because of this 'moving boundary' problem. For example, this work was started with a literature survey that was completed in the early 1986. Even as we proceeded, we have tried to update the information to the extent possible. In spite of all these efforts, we notice many recent developments that could have been included. If we are to cover all these new developments, we may have to present the appendix in the form of another small book and keep on adding those small books one after another—an impossible task! We shall however try to briefly sketch the new developments that are taking place in recent times with some futuristic perspectives. We have also tried to collect some monographs, edited books and critical reviews that have appeared during the past two or three years but did not find place in the appropriate chapters due to time lag. We have only covered the recent fundamental and electroanalytical literature here. The rate of growth in different electrochemical technologies and electrochemical engineering disciplines is even higher. The frontiers of electrochemistry are moving fast indeed!

17.2 THE MODELS AND METHODS

The basic outline of interfacial electrochemistry presented in this work (Chapter 1) has not undergone any drastic change in the short period under review. The investigations on the structural (double

layer) aspects are growing faster making up many new grounds. In addition to Hg, many other active metals such as Ga, Bi, Pb and noble metals such as Au and Ag are being investigated in detail through capacitance measurements. In the modelling side, there is growing orientation towards molecular models from the hitherto common phenomenological models. The importance of metal surface in the overall interfacial capacitance behaviour is being realized and efforts are being made to develop a model where metal surface as well as the solvent surface effects are correctly accounted for. Two recent volumes vividly bring out the recent developments in the interfacial science [1] and the research and development efforts [2] in the field of electrochemistry covering structural as well as dynamic aspects of interfacial processes.

After a lapse of several years, some monographs on general aspects of electrochemistry are again appearing [3, 4]. But once again, the emphasis is on solution phase processes along with the implicit assumption of inert electrodes serving as source or sink of electrons (In the pattern of Part B of the present work). We hope and wish that the general electrochemistry curriculum becomes much more realistic and present a broader view of the entire spectrum of electrochemistry. The sooner this happens, the better for electrochemistry. One interesting recent addition [5] gives a more comprehensive picture of electrochemistry by covering the electrocrystallization and electrocatalytic aspects although the name of the book suggests that it is about instrumental methods.

In this work, we have heavily relied on phenomenological modelling of interfacial processes. Much of the present day understanding of electrochemistry is certainly due to this level of modelling. Our ability to comprehend multicomponent systems even at this level is far from complete. However, there is certainly need for modelling at the higher levels, viz. molecular, statistical mechanical and quantum mechanical modelling of electrochemical processes. We should certainly catch up with other branches of physical chemistry. Although there are some activities on these lines, the progress is certainly very slow. A recent text book on theoretical electrochemistry tries to develop the subject on a molecular basis [6]. However, the overall task is still incomplete. The work has just started rather.

In addition to the analytical bias in the text books mentioned

above [3-5], some new works primarily oriented towards electroanalytical chemistry have also appeared. Comprehensive treatments of electroanalytical methods for general purpose [7,8] and special purpose [9] applications are described in detail. A laboratory guide on instrumental methods published a little earlier [10] also contains some excellent practical information on electroanalytical methods. However, in the electroanalytical chemistry, we have still not come out of the 'inert electrodes' and the 'electrochemistry of ions and molecules in solution' syndrome. All the electroanalytical methods that are available can in some way or other be employed for other processes as well (Parts C, D, E of this work). It is necessary that our electroanalytical texts also emphasize this aspect. A recent book deals with electrochemical and non-electrochemical methods employed in electrochemical research [11]. This is certainly a welcome move. This work also contains a useful collection of classified electrochemical literature.

Although the literature on almost all branches of electroanalytical chemistry is growing at a faster pace, very rapid developments are noted in at least four directions. Electroanalysis in flowing liquid systems is very useful for on-line monitoring of many electrolytes and in the electrochemical detection in HPLC [12]. Ultramicroelectrodes can be used as single strands or as collections. The mass transfer effects are minimized to a great extent on these electrodes. This method has created great enthusiasm in the past couple of years [13]. Electrochemical sensors [14-16] especially biosensors [15, 16] is another area that attracts great interest. A separate journal on biosensors has started appearing [17]. Most of these biosensors are electrochemical in nature. Both potentiometric and voltammetric sensors are in use. Spectroelectrochemical methods are also becoming quite popular in recent times [11]. These developments in the past few years should be enough to shed off any opinion that 'electroanalytical methods have all been developed and exhausted already'.

17.3 SOLUTION PHASE PROCESSES

As we have been pointing out throughout this review, the solution phase processes are finding their share—or more than what they deserve rather—in all the electrochemical text books that have

already appeared and those appearing in recent times. It is the other components (see later) that require greater attention.

The redox equilibrium of most of the processes where both the reactants and products are stable are now well-documented. A recent publication, for example, gives the standard electrode potentials of all the elements in different oxidation states [18] in aqueous solutions. Investigation of complex formation equilibria, one of the classical application area of polarography, is still being reported, from time to time. But this type of studies have become so common and so routine that some journals specifically state that they will not accept any stability constant determination type of work for publication. Equilibrium measurements of biological molecules and organometallic systems and solvent effects on redox equilibrium are some of the areas that stimulate active interest. Measurement of equilibrium properties of redox reactions involving highly reactive intermediates is another challenging area of current electrochemical research where cyclic voltammetry is used (Chapter 5).

The theory of electron transfer kinetics still remains to be the hottest topic in electrochemistry. Books [19] and monographs [20, 21] continue to appear in this area. New methods for treating outer-sphere as well as inner sphere electron transfer are being discussed [22]. However, the distance between quantitative calculations of rate parameters and their experimental verification still lies far apart. A recent review [21], for example, shows that even a simple electron transfer reaction should be assumed to consist of 'many steps' that contribute to the overall rate. At present, it appears that we are trying to develop a very detailed model at the quantum mechanical level for use in an experimental situation that is too complicated and inaccurate. However, the efforts to link up the theory and experiment in the 'comparative' level still continues. A recent monograph discusses this methodology for organic electron transfer processes in some detail [23].

The voltammetric methods for the study of chemical reactions associated with charge transfer have developed quite extensively (Chapter 5). In fact, the methods have grown much faster than the actual applications. We may also mention one or two interesting developments here. Multisweep cyclic voltammetric method is being used to investigate ECE mechanism involving the formation of more easily oxidizable or reducible species that give rise to volt-

ammetric peaks in the second and subsequent sweeps (Chapter 5). The quantitative simulation of cyclic voltammetric curve for such multisweep situation has been achieved recently [24]. Electron transfer to or from a strained cyclic molecular system can cause interesting geometric transformations which were reviewed recently [25].

Voltammetric methods have become a very common tool in the development of electro-organic processes as one would realize by turning through the pages of a recent proceedings [26]. In a recent electrochemistry text book, voltammetric examples from organometallic chemistry are extensively quoted [3]. In addition to these traditional areas, voltammetric methods also find place in the study of biomass and related products [27].

17.4 SURFACE PROCESSES

All electron transfer processes are essentially interfacial processes or in a general sense, surface processes. However, we have used the term 'surface processes' in this text to denote those processes where there is a chemical change on the surface such as metal dissolution, phase formation, growth or change in the redox properties of surfaces.

Among the surface processes, the metal-dissolution phenomena have received some detailed attention [28]. Stripping voltammetry (Chapter 6) is gaining greater acceptance. The adsorptive stripping method perhaps can be applied for the analysis of many organic compounds although it loses the specificity of cathodic or anodic stripping voltammetry [29]. The electroplating industry has also taken note of the use of cyclic voltammetry for continuous monitoring of electroplating solutions. They employ the so-called 'cyclic voltammetric stripping' method [30] and 'cyclic pulse voltammetric stripping' method [31] which are essentially stripping voltammetric methods with slight differences in the preconcentration steps. These techniques are likely to become the major watchdogs in the automatic high precision electroplating plants of the future.

Monolayer formation (Chapter 7) and monolayer redox processes (Chapter 9) are investigated using almost identical voltammetric methods. In the planning of this monograph, the possibility of treating these two processes together was considered. The present

arrangement was retained just to retain the clarity at the conceptual level. These two processes are good examples of two different models leading to quite similar methods of analysis. Redox monolayers (Chapter 9) probably cannot serve as efficient catalysts (Chapter 13). The monolayer formation-dissolution processes (Chapter 7) are being investigated with increasing precision on well-defined surfaces with more sophisticated ultra high vacuum techniques because of their probable electrocatalytic applications (Chapter 13).

Thin layer formation and growth processes are much more important for electrochemical technologies such as electrometallurgy, electroplating and electrochemical corrosion protection (Chapter 8). However, because of the number of phenomenological components involved, these processes are not amenable to investigation even at the model level. There does not seem to be any serious effort in this direction in the recent past. Even the equivalent circuit analysis in impedance spectroscopy does not offer much answer to the 'why' side of the story. In our opinion, this is one of the challenging areas of electrochemistry which requires further attention primarily at the modelling level.

Investigations on conducting polymers now dominate the field of thin layer redox processes. Good reviews on redox polymers [32] and conducting polymers [33] continue to appear. In addition to the electronically conducting polymers investigations on ionically conducting solid polymers like polyethylene oxides are receiving greater attention in recent times [34, 35]. Cyclic voltammetric methods have been used for investigating such solid state electrode-electrolyte interfaces as well [36]. These new developments would certainly lead to further research in the near future.

17.5 CATALYSIS AND INHIBITION

Catalysing important electrochemical reactions such as H_2 , Cl_2 , O_2 evolution and O_2 reduction continue to attract great interest. Recently, electrochemists have also ventured into the very ambitious project of catalysing electrochemical reduction of nitrogen. In spite of such an amount of enthusiasm, not a single uniform monograph on electrocatalysis has emerged. Most of the books on electrocatalysis now available are conference proceedings. However, the original

research in this field is indeed growing very fast. Surface structure and electrocatalytic behaviour of carbon electrodes [37] have been reviewed recently. A recent review on oxide electrodes has also appeared [38]. A monograph that does not bring any new insight into the concept of electrocatalysis has also appeared [39]. A uniform and rigorous development of concepts of catalysis in the electrochemical context is urgently needed for more consistent development in this area.

In part D, we have tried to develop the concept of electrocatalysis in a systematic manner based on the types of electrodes involved. Combining these ideas, we can propose the following general outline for electrocatalysis.

The stability and good electronic and ionic conductivity of the electrode surface is the primary requirement of electrocatalysis.

It would be desirable to have as much active surface area as possible for a good overall electron-transfer rate. Although these two factors do not physically constitute electrocatalysis, these requirements are basic for any efficient electrocatalyst development.

Three physico-chemical lines of electrocatalysis can be distinguished although there can be interconnections. The electrodes can show redox catalysis if they can exhibit multiple oxidation states and the redox reaction rate between the catalyst and substrate are fast. The electrocatalysis may also be due to the acid-base properties of the electrode surface. The acidic surfaces would generally catalyze reduction and the basic surfaces would catalyse oxidation. If the surface of the electrode does not contain high level of electrostatic polarization, the electrocatalysis proceeds through adsorbed intermediates. In this case, the electrocatalysis is due to electrochemisorption effect.

We hope that these concepts would receive further evaluation and development in the future.

17.6 PHOTOELECTROCHEMISTRY

Photoelectrochemistry is certainly growing at a very fast pace today. New publications in this area include lecture notes [40] on general aspects of photoelectrochemistry, a review of mathematical models and concepts [41] and a collection of experimental data on different semiconductor electrodes [42].

In the experimental side, the photodecomposition of water still remains to be the reaction of primary interest. However, an increasing number of research work now concentrates on CO₂ reduction, the primary process in photosynthesis, and the N₂ reduction, the primary reaction in biological nitrogen fixation. Although molecular photoexcitation is still being investigated with great enthusiasm (Chapter 15), the semiconductor photoexcitation certainly offers greater potential of success. However, further success should certainly come from the investigations of surface chemistry and catalysis. As we have emphasized earlier (Chapter 16), photoelectrochemistry today relies too heavily on semiconductor physics and some recent developments certainly suggest that there would be a welcome reversal of trends in this regards.

17.7 TOWARDS THE FUTURE

We have briefly sketched the moving frontiers of electrochemistry. More than anything else, we have tried to emphasize the dynamism growth and change in the field. The advances and gaps in different branches of this field were also pointed out. And so this is the situation today (early 1989). Many changes are likely tomorrow. Where shall we go from here?

We can be very optimistic about the future if the recent developments serve as the right indication. With the availability of the modern computers, we can conceive of realistic models and their accurate mathematical representations, and we can certainly analyse the model behaviour by simulation techniques. Great strides can naturally be expected in all the hierarchical levels of modelling, namely phenomenological, molecular, statistical mechanical and quantum mechanical levels. These developments would certainly be matched by the emerging advances in the analytical techniques. In addition to the classical and the newly developing electroanalytical techniques, we may rely heavily on the non-electrochemical techniques such as spectroscopic, microscopic and diffraction techniques for a thorough understanding of the electrode surface and its electrochemical activity. We may be able to analyse the interface, atom by atom or molecule by molecule, using frontline analytical techniques such as scanning tunnelling microscopy [43-45]. The models and methods so developed would be used to investigate and improve

the electrochemical systems in so many ways for the welfare of mankind.

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