Electrochemistry in Research and Development

Edited by
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Plenum Press • New York and London

Library of Congress Cataloging in Publication Data

UNESCO Forum on Electrochemistry in Research and Development (1984: Paris, France)
Electrochemistry in research and development.

"Proceedings of the UNESCO Forum on Electrochemistry in Research and Development, held June 3-6, 1984, in Paris, France" – T.p. verso.
Includes bibliographies and index.
1. Electrochemistry – Congresses. I. Kaldova, Robert. II. Parsons, Roger. III. Title.
QD551.U54 1984 541.3′7 85-30067
ISBN 0-306-42219-0

Proceedings of the UNESCO Forum on Electrochemistry in Research and Development, held June 3-6, 1984, in Paris, France

A Division of Plenum Publishing Corporation
233 Spring Street, New York, N.Y. 10013

Printed in the United States of America

PREFACE

This volume contains the papers presented at the UNESCO Scientific Forum on Chemistry in the Service of Mankind - Electrochemistry in Research and Development, held in Paris, June 4-6, 1984.

Electrochemistry is concerned with the way electricity produces chemical changes and in turn chemical changes result in the production of electricity. This interaction forms the basis for an enormous variety of processes ranging from heavy industry through batteries to biological phenomena. Although there are many established applications, modern research has led to a great expansion in the possibilities for using electrochemistry in exciting future developments. To encourage this progress, UNESCO has set up an Expert Committee on Electrochemistry and its Applications in the European and North American region, which has already held a number of meetings devoted to specific topics. To achieve a synthesis of the main directions of development and to demonstrate the importance of these for the needs of our modern society, the Expert Committee organized a Forum on Electrochemistry in Research and Development.

The object of this was to assess the future trends in research and development and to establish a dialogue between experts in electrochemistry and their colleagues in the many other disciplines which can make use of electrochemistry. The Forum was also intended to present electrochemistry and its applications in a form accessible to non-specialists so that science policy-makers will be aware of the potentialities of this subject for the future needs of mankind.

The program of the Forum included four sections with plenary lectures followed by discussion on the following topics:

Electrochemistry and

- Energy - Solar Energy Conversion
  Energy Conversion and Storage
  Hydrogen Economy

- The Environment - Analysis and Removal of Pollutants
  Trace Metal and Analysis
  Food and Drug Control

- Biosciences — In Vivo Applications
  Membranes
  Genetic Engineering
  Polymer Electrodes

- Technology — Potentialities in New Technologies
  Processes in Chemical Industry

Prof. A. A. Vlček, the Chairman of the UNESCO Expert Committee on Electrochemistry for the European and North American Region, was in the chair: about 140 visitors attended the meeting.

R. Kalvoda
R. Parsons

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GENERAL INTRODUCTION I

A. A. Vlček

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Electrochemistry is an interdisciplinary science, combining mainly chemistry, physics, solid state science and electronics, of immense theoretical and practical importance.

This special interdisciplinary position of electrochemistry led, on one side, to its development as an almost independent branch of science, on the other hand has caused a certain isolation of electrochemistry from chemistry, where its roots come from. This isolation can be for example demonstrated at universities as well as on the position of electrochemistry in industry. Very few universities teach a proper course of electrochemistry, and if so, then mainly oriented toward electroanalytical applications or as a minor part of physical chemistry.

In industry there is, on one side, a huge application (batteries, galvanoplating, heavy inorganic technology) with its specific technologies, on the other side; there are very few examples of electrochemical procedures used in integrated technologies. As the most recent example of the latter, use of electrochemistry in the industry of semiconductor devices can be quoted. However, the potentialities of electrochemistry are much wider but the R and D people, and especially those designing new technologies, are rarely aware of them.

Electrochemistry as science per se formulates very fundamental questions and problems and develops a basis for interpretation of many phenomena of nature. The basis electrochemistry has developed is such that electrochemical methods can be used as a standard method in chemical research when investigating redox properties or structure of inorganic and organic compounds. Electrochemical methods of preparation can provide unusual species hardly accessible by other techniques. Again, due to the specific nature of electrochemistry not always are research people in other branches aware of electrochemical results and possibilities of their application in other scientific discipline. As an exception, electroanalytical chemistry can be mentioned. Methods of electroanalytical chemistry are widely used in the control of industrial processes, monitoring of environment, biology, clinical chemistry etc.

All these reasons led in 1977 to the decision to establish an international cooperation in electrochemistry on a UNESCO basis. The main goal of this cooperation has been to bring electrochemists into closer cooperation, to specify the most urgent problems and future lines of development of electrochemistry and last but not least to make scientists and R and D people more aware of the possibilities electrochemistry offers, or might offer in future, in solving scientists tasks as well as problems for the development of new technologies.

This main idea of cooperation, the results of which, will be mentioned in the contribution by Prof. Gierst, represents also the chief motive which led to the decision to organize this Scientific Forum on Electrochemistry in Research and Development. At the same time we have hoped to increase the awareness of electrochemists of the necessity to make a greater offer in getting their results more widely known and used.

GENERAL INTRODUCTION II

L. Gierst

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UNESCO works in a world-wide framework aimed at promoting education, science and culture. In this it has quickly become aware of the fact that Electrochemistry is a particularly fertile domain with far-reaching potentialities; they extend well beyond its academic frontier and have important implications in economic and social matters.

As a first step, a meeting of experts, working on the general theme "Perspectives in Electrochemistry" was held in Prague in March 1977. The multifarious subdisciplines of Electrochemistry were appraised critically and a limited number of fields were selected as more likely than others to lead to significant and fruitful developments.

The delineation of priority fields came as the logical result of a convergence between criteria of purely scientific nature and the fundamental background of the UNESCO philosophy. One of the major concerns of this philosophy is to promote the exchange of information (cultural, educational as well as scientific) into the whole world, irrespective of artificial barriers of any possible nature. This involves giving help in disseminating knowledge as soon as it is acquired, and taking the decisive steps that could answer the most pressing needs of society, perceived locally as well as on any broader scale. This necessity implies a totally new approach in the scientific, technological and educational ways of defining domains of action, through the creation of new types of relationships between pure science, its educational vehicles, the research laboratories, the electrochemical industry and society itself, with its growing awareness of the need of upgrading the level of knowledge, in its everlasting struggle for better material conditions and increasing quality of life. For this to work smoothly and efficiently, the free flow of information and the dissamination of new findings would profit by being channelled through adequate facilities, in order to coordinate the efforts on a regional or a world-wide base, to stimulate the rate of mutual exchanges, with the additional bonus of lowered running costs.

But let us return to Electrochemistry. The expert committee of UNESCO, on the basis of thorough critical exploratory work, reached the conclusion that three main areas for research and training should be retained as the major lines of force of the program.

Project one deals with electrochemical energy conversion and storage, with special emphasis on photoelectrochemistry, on the methodology of electrochemical storage and on the synthesis of energy-rich compounds. This project has been vigorously pursued in recent years, with three international workshops, successively dedicated to Electrochemical Energy Conversion, Photoelectrochemistry and High Energy Density Light Metals. Three other meetings, already scheduled, will focus on Photoelectrochemical Processes, Modified Electrodes, Solar Energy Conversion and New Developments in Conversion and Storage.

The second project considers electrochemistry in its relations with environmental problems. The two major topics are the development of electrochemical monitors specially adapted to pollution, and the electrochemical removal of environmental pollutants, these processes can be made economic and highly selective. Three successive workshops have already been devoted to these topics, with special emphasis on electrochemical sensors in water analysis.

The third project is concerned with the electrochemical aspects of materials, taken in their broadest sense. It includes electrode interfaces, adsorption layers, bioelectrochemistry and the huge field of electro-organic synthesis. This project has resulted up to now in five workshops, the accent being put on organic electrochemistry and the behavior of interfaces.

These three series of workshops have led to significant results, judged not only from a strictly scientific point of view: a number of laboratory networks have been established, informal cooperative research has started and most of the available research facilities have been surveyed. Rapid exchange of information has been enhanced by facilitation of short visits, microsymposia and contacts with young scientists from developing countries. Most of these activities, including the workshops, have been strongly catalyzed by the action of the UNESCO coordinating group, with the help of UNESCO funds supplemented by local contributions from governmental and private organizations.

It is perhaps still somewhat premature to assess the full impact of the UNESCO program, as it is felt by the electrochemical community and society. It is clear, nevertheless, that the direct and fast flow of information, the formation and strengthening of flexible scientific networks and the exchange of collaborators have resulted 1) in stimulating ideas, 2) in enhancing the pace of dedicated research, 3) in extending the use of underemployed equipment and 4) in conducing to a better based selection of specific research topics. These positive efforts are leading to a better use of all available means, human as well as technical. This will contribute to more efficient fund distribution and utilization by discouraging too-redundant programs and by easing a part of the routine work.

The organizing committee, from the very start of its activities, has been fully aware that science in general, and Electrochemistry in the present case, is a matter which concerns the whole planet. In order to promote dissemination of Electrochemical Science, taking account of the basic needs of the Society. It has been decided to launch an additional project, devoted to the publication of a book on "Teaching in Electrochemistry". The major objective here is to allow any teacher working far from a suitable educational center to construct his own course of electrochemistry, with minimal demands in equipment. This book is organized in such a way that full coverage of the Electrochemical Science will be presented at three different levels of qualification. This structure will allow the teacher to adjust his training course to the average background of his class, taking into account the local availibility in materials and equipment.

Besides these various activities (coordination work, specialized workshops, joint projects, educational aspects, etc.) the organizing committee felt compelled to set up the present meeting. It has been appropriately called a "FORUM" in the sense that its major objective is to trigger off an effective interaction between Science and Society, by bringing together specialists in Electrochemistry and non-specialists who are well aware of the pressing need to raise the level of knowledge, but are uncertain about the routes to follow. They know that enhancement of this knowledge constitutes one of the firmest bases of action for improving living conditions.

Human implications will thus be constantly present among us, particularly perhaps in relation with the developing countries where Science and Technology, after suitable adaptation, remain the best hope for economic as well as social improvements. UNESCO successfully manages to bring the scientists of the developing countries into closer and closer contact with the laboratories of the more industrialized countries, in order to afford, in this way, a simpler and more economical access to scientific know-how than was the case in the past and still is at present. Its constitutional bylaws allow UNESCO to assume a privileged role among other international organizations, in its capability of helping scientific progress by direct aid, coordination, stimulation and crossfertilization between adjacent fields. Electrochemists are not automatically fully aware of the problems and needs of the Society, either at local and regional or world-wide level. Conversely, people who have a better perception of these problems but are not dedicated to scientific research may lack the degree of expertise required for taking appropriate decisions - which may sometimes involve millions of individuals. By asking specialists to assess the state-of-the-art and the perspectives in their respective fields, and by offering ample time for debating with the audience, the organizing committee is convinced that a new type of communication bridge will be built and that a far-reaching dialogue will develop and become firmly established. It will be an exciting and unique experience.

We are particularly glad to express our thanks to all the participants, who have shown their dedication to the problems which will contribute the core of this FORUM. More particularly, we express our gratitude to the UNESCO authorities, to the lecturers for their care and help and to the chairmen who have reacted enthusiastically to the perspective of sharing the efforts of the organizers and are ready to make this meeting as relevant and fruitful for as many people as possible.

We are also convinced that those of us who will attend the three days of this FORUM will not, afterwards, disperse to the four cardinal points, without seizing the present opportunity to confirm durable and enriching contacts.

Whether in Science or in Social development, the main tasks are still ahead of us. Working closely together will increase our force and strengthen our determination.

INTRODUCTORY TALKS

WHAT IS ELECTROCHEMISTRY ?

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INTRODUCTION

The science of electrochemistry was born at the end of the eighteenth century following intense interest in the production of electricity by animals such as the torpedo and the electric eel. The key phenomena were observed just at the turn of the century. Volta invented his pile in which chemical species were consumed with the production of electricity and a few months afterwards Nicholson and Carlisle used this electricity to decompose water into hydrogen and oxygen. It is this two-way process which lies at the heart of electrochemistry; it may be represented by a very simple diagram

$$\text{Electricity} \underset{\rightarrow}{\leftarrow} \text{chemical compounds}$$

which hides the many complexities of this interchange. One might imagine that study of a branch of science over nearly two centuries would exhaust its interest and its potentialities but this is far from being so. Electrochemistry continues to find new applications in wider fields as well as providing scope for greater understanding of its fundamentals. A brief and rather selective outline of the history of the subject should illustrate this as well as the range of its interest.

NINETEENTH CENTURY

The first half of the century was dominated by the work of Davy and Faraday. Although they both made many fundamental discoveries, they were always interested in practical applications. Thus Davy used electrolysis to discover the alkali metals but also applied his electrochemical knowledge to suggest cathodic protection to the Royal Navy as a way of preventing the corrosion of their copper-sheathed wooden ships. Corrosion remains a major problem today. It was estimated that losses due to corrosion cost the United States 4½% of the GNP or about $70,000 million per year in 1975.

Faraday showed that all known forms of electricity were identical and then discovered the quantitative relation between the electric charge passed through a cell and the amount of chemical change which occurs. These observations are nowadays easily understood because an electrical current in a metal is known to be a stream of electrons. He laid the basis for electrochemical terminology and also for the understanding of passivation which plays such an important role in the protection of materials.

Not long after Faraday's electrochemical work, Sir George Grove in 1842 showed that Nicholson and Carlisle's experiment of the decomposition of water could be reversed, that is, hydrogen and oxygen could be combined to form water, in an electrochemical cell, with the production of electricity. Besides giving a complete and simple demonstration of the primary electrochemical process, this was important because it led the way to a fuel cell in which a fuel, hydrogen, could be continuously oxidized electrochemically in contrast to the cells derived from Volta's pile which have a capacity limited by the amount of active chemical contained in them. Grove's fuel cell was the forerunner of the hydrogen-oxygen fuel cells used in the Gemini and Apollo space capsules. In fact Grove used his cell already in 1842 with primitive incandescent lamps to light the lecture theatre of the London Institution.

Developments of Volta's pile which are known as primary batteries, were made during the nineteenth century. The most enduring is the cell invented by Leclanché in 1867 in which zinc dissolves at the anode and manganese dioxide is reduced at the cathode. This basic principle is still used in many of the dry cells which are the familiar power sources for portable electronic apparatus like radios. These cells are essentially irreversible; one cannot recharge them, so once the electroactive material is consumed they are usually thrown away. Rechargeable cells or secondary batteries are more economical and the best known of these is the lead accumulator invented by Planté in 1860. It is now used in every automobile to power the starter motor and as an energy reservoir as well as being the sole power source in the majority of electric vehicles. Electricity is produced from the reduction of lead dioxide to lead sulphate and the oxidation of lead to lead sulphate and these processes are reversed on charging the battery. Fundamentally the working of this battery depends on the properties of lead which can exist in three states of oxidation each step requiring the transfer of two electrons and also on the fact that suitable solid compounds of lead are available. This simplifies the practical achievement of the battery although not the detailed explanation of its operation.

Humphry Davy's use of electrolysis using molten electrolytes to produce active metals culminated near the end of the century in the industrial production of aluminium on the basis of the independent discoveries by Hall and Héroult in 1886 that alumina could be electrolyzed in a molten cryolite bath.

The intense activity in electrochemistry in the nineteenth century covered both fundamental and practical aspects, but although it was established early that the process itself was one which occurred at the junction between a metallic and a non-metallic conductor. Little progress was made in the basic understanding of this reaction. To a large extent this was because the nature of the conduction of electricity itself was poorly understood and such understanding developed in parallel with the development of electrochemistry itself. In fact, the idea that an electric current always consists of a flow of charged particles replaced the idea of an "electric fluid" gradually during the century and was only firmly established by the discovery of the electron by J. J. Thomson in 1897 and the proposition of the ionic theory of electrolytic conduction by S. Arrhenius in 1187. Thus it became clear that the basic electrochemical event was a result of the change in the mode of conduction of electricity, from the flow of the minute, negatively charged, electrons as in a metal to the much larger and heavier charged particles which could be identified