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# Condensed Matter Physics Aspects of Electrochemistry

PROCEEDINGS OF THE CONFERENCE

# Condensed Matter Physics Aspects of Electrochemistry

27 August – 9 September 1990  
ICTP, TRIESTE, ITALY

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**World Scientific**

Singapore • New Jersey • London • Hong Kong

P 9210/18

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电化学的凝聚物质物理学观点

(英2-4/7366)

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A 02340

Published by

World Scientific Publishing Co. Pte. Ltd.

P O Box 128, Farrer Road, Singapore 9128

USA office: Suite 1B, 1060 Main Street, River Edge, NJ 07661

UK office: 73 Lynton Mead, Totteridge, London N20 8DH

## CONDENSED MATTER PHYSICS ASPECTS OF ELECTROCHEMISTRY

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ISBN 981-02-0560-0

Printed in Singapore by Utopia Press.



## PREFACE

This volume collects the proceedings of the Working Party on "Electrochemistry: Condensed Matter, Atomic and Molecular Physics Aspects", held for two weeks in the summer of 1990 at the International Centre for Theoretical Physics (ICTP) in Trieste. The goal of the meeting was to discuss those areas of electrochemistry that are accessible to the modern methods of theoretical condensed matter, atomic and molecular physics, in order to stimulate insight and deeper involvement by theoretical physicists into the field.

What is particularly interesting for a physicist in Electrochemistry? The answer one may find by reading some earlier reviews and conference proceedings<sup>1-8</sup>. The correct answer should start with the importance of the field in itself. A beautiful answer has been given by Frumkin in his scientific testament, "a word in favor of electrochemistry"<sup>9</sup>. Here, we wish to stress two main points.

Electrochemistry is a science with important technological applications. These are, in particular:

- Energy conversion and power sources
- Transducers of information signals
- Electroanalysis
- Materials processing
- Electrolysis, electrocatalysis and electrosynthesis
- Inhibition of corrosion
- Biomedical engineering (heart stimulators, artificial kidney, acceleration of bone mending etc.).

The roots in the fundamentals of other sciences are no less important. Electrochemistry underlies many phenomena in inorganic chemistry, colloid science, biophysics and biochemistry. It is a powerful partner in a number of problems in the physics of liquids and solutions, solid state physics, surface science.

Electrochemistry and "electrophysics" developed hand in hand from the first steps in the study of electricity. The names of Galvani, Volta and Faraday are usually cited in this

1. H. Gerischer, D. M. Kolb and J. Sass, *Adv. Phys.* **27** (1978) 437.
2. *Nontraditional Approaches to the Study of the Solid-Electrolyte Interface*, eds. T. E. Furtak, K. L. Klierer and D. W. Lynch, *Surf. Sci.* **101** (1980).
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4. *Studies in Physical and Theoretical Chemistry*, eds. W. H. Hansen, D. M. Kolb and D. W. Lynch, vol. **29** (Elsevier, Amsterdam 1983).
5. *Electrodynamics and Quantum Phenomena at Interfaces* (Mezniereba, Tbilisi 1986).
6. *Structure and Dynamics of Solid/Electrolyte Interfaces*, eds. H. Gerischer and D. Kolb, *Ber. Bunsenges. Phys. Chem.* **91**(4) (1987).
7. *Chemistry and Physics of Electrified Interfaces*, ed. S. Trasatti, *Electrochim. Acta* **34**(12) (1989).
8. *Interdisciplinary Conference on Electrified Interfaces*, eds. D. Henderson and O. Melroy, *Electrochim. Acta* (1991) in press.
9. A. N. Frumkin, *Selected Works: Electrode Processes* (Moscow, Nauka 1987) p. 24.

context. The best example from the present century is the Debye theory of electrolytes, which has had an enormous impact on many-body physics. The fundamental equation of electroanalysis, i.e. the Lippmann-Gibbs equation, is the basic formula of electrocapillarity (as discussed in the Landau-Lifshitz book on Electrodynamics of Continuous Media). This list could be continued.

The next round of impetuous compenetration of these sciences, which began in the seventies, was induced by the "surface science boom". It was recognized that interfacial electrochemistry provides a number of possibilities for the study of metal or semiconductor surfaces *in situ*, i.e. in contact with the electrolyte. The latter plays a twofold role. The experience in "clean electrochemistry" allows one to deal with a solution instead of vacuum almost at an equivalent degree of purity. Secondly, and most importantly, the metal in contact with the electrolyte can be strongly charged by applying a moderate voltage, owing to the very large interfacial capacitance. A new and well controlled variable thus appears in the system. Moreover, the electric field produced by this charge is localized - due to screening by the electrolyte - within a thin interfacial region. Hence, the response to charging probes just the properties of the interfacial region.

The core of the ICTP Working Party was a set of topically grouped plenary lectures, accompanied by contributed seminars and by the formulation of joint research projects. In the tradition of the ICTP, it was not a meeting of pure theoreticians: about half of the lecturers were professional experimentalists - experts in electrochemistry, physical chemistry, surface science, technical applications. A finite set of topics was chosen for discussion at the meeting:

- Liquids, solvation, solutions
- The interface (structure, characterization, electric properties, adsorption)
- Electrodynamics, optics, photo-emission
- Charge transfer kinetics (homogeneous and heterogeneous reactions and processes)
- Superconducting electrodes
- Fractal electrodes
- Applied research (energy conversion and power sources, electrocatalysis, electroanalysis of turbulent flows).

A number of important directions in modern electrochemistry are still missing from this list. These are various aspects of hydrodynamics and mass transfer, diffusion and migration processes, multi-stage reactions, chaos and dissipative structures, superionics, bio-electrochemistry.

It was a common view of the participants in the meeting that its main fruit, which is a coherent picture of a large part of theoretical electrochemistry as a "condensed matter science", was worthy of record. In order to achieve a thorough analysis of the state of the art, it was also necessary to address some long-standing questions, which are often passed by because of their complexity and lack of sufficient knowledge. To create a background for an approach to such problems, some of the lecturers were welcomed to speak about matters that they had already reviewed in their publications. Such contributions are present in this volume as extended abstracts or brief notes, with updated references. In fact, the

special character of the ICTP Working Party makes this book closer to a collective monograph than to typical conference proceedings.

In conclusion, we wish to acknowledge the support of Professor Abdus Salam and of the ICTP Solid State Advisory Committee, especially Professor Stig Lundqvist and Professor Norman March. We thank all who contributed to the scientific outcome of the Working Party: the lecturers (whose talks were deep, comprehensive and exciting) and the participants (whose questions, seminars and enthusiasm stimulated the work). Special thanks are due to the ICTP secretarial staff, particularly to Ms Deisa Buranello and Ms Marina De Comelli. One of us (A. A. K.) acknowledges the support of his regular visits to the ICTP given by the A. N. Frumkin Institute. His contribution to the final editorial process was facilitated by his stay at the Technical University of Munich as a Humboldt Award Guest Professor (Humboldt Foundation, FRG).

Alexei Kornyshev and Mario Tosi  
Moscow-München and Trieste

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## APPLIED RESEARCH

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# INTRODUCTORY NOTES

Electrochemistry is an interdisciplinary science. Its understanding combines chemistry, particularly structural and kinetic chemistry and physical chemistry, electrostatics, electrodynamics and solid state physics. It also has close links with other sciences. In this lecture the interrelation with physics have been exemplified. Some recent developments which have stimulated progress in both chemistry and physics have been chosen, for which a selection of references is given at the end of the lecture.

## 1. General Properties of Electrodes and Adsorption from Electrolytes

The chemical composition of the interface can now be analyzed by new spectroscopic techniques which have been developed in surface physics under ultrahigh vacuum (UHV) conditions. Some of them can only be applied ex-situ after transfer of the electrode into UHV. Other techniques in which the signal can pass the electrolyte have been developed in-situ.

In-situ methods are particularly photoelectron emission and electron energy loss spectroscopy (Auger PS, UPS, XPS, EELS) 1-4 and electron diffraction techniques (LEIS, ED) 2,3,7-10.

Other techniques do not include the risk that the surface composition or structure is changed during the transfer into the vacuum. They can also be applied in-situ on electrodes. Particularly instructive for the adsorption of organic molecules is IR reflection spectroscopy 11,12, in some special cases Raman reflection spectroscopy 13,14. Information on electronic properties of electrode surfaces and their interaction with surface composition or electrode potential can be obtained from electrochromic spectroscopy with visible or UV light 15-17. Finally, X-rays can also be used



Source: *Journal of Applied Physics*

M. W. G. G. G.

Turbulent Mass Transfer in Electrochemical Systems

Turbulence in Electrochemical Systems

# INTRODUCTORY NOTES

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## ELECTROCHEMICAL PHYSICS

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### Abstract

In this contribution, areas are emphasized, where the concepts of physics are fundamental for the interpretation of electrochemical processes or new techniques, developed in physics, have promoted the understanding of such processes. The short text and the references may be used as a guide to more detailed information.

### 1. Introduction

Electrochemistry is an interdisciplinary science. Its understanding combines concepts of chemistry, particularly structural and kinetic chemistry and physics, especially electrostatics, electrodynamics and solid state physics. It also has close links to biology. In this lecture the interrelation with physics have been exemplified with emphasis on some recent developments which have stimulated progress in both fields. Three general topics have been chosen, for which a selection of references is given in the following.

### 2. Surface Properties of Electrodes and Adsorption from Electrolytes

The chemical composition of the interface can now be analyzed by new spectroscopic techniques which have been developed in surface physics under ultrahigh-vacuum (UHV) conditions. Some of them can only be applied ex-situ after transfer of the electrode into UHV. Other techniques in which the signal can pass the electrolyte can be used in-situ.

Ex-situ methods are particularly photoelectron emission and electron energy loss spectroscopy (Auger PS, UPS, XPS, EELS) <sup>1-6</sup> and electron diffraction techniques (LEED, RHEED) <sup>2,3,7-10</sup>.

In-situ techniques do not include the risk that the surface composition or structure is changed during the transfer into the vacuum. They can also be applied for dynamic processes at electrodes. Particularly instructive for the adsorption of organic molecules is IR reflection spectroscopy <sup>11,12</sup>, in some special cases Raman reflection spectroscopy <sup>13,14</sup>. Information on electronic properties of electrode surfaces and their variation with surface composition or electrode potential can be obtained from reflection spectroscopy with visible or UV light <sup>15-17</sup>. Finally, X-rays can also be used

in-situ for monolayer and surface studies where a high intensity source from synchrotron radiation is available. With grazing incidence of the X-rays and small variations of the angle of incidence one can obtain structural information <sup>18,19</sup>. The analysis of the interference with neighboring atoms reveals distances in adsorbates or in the electric double layer (EXAFS) <sup>20,21</sup>. A most recent technique giving structural information about the electrode surface in-situ up to atomic resolution is scanning tunneling microscopy (STM) <sup>22-24</sup>.

### 3. Influence of Solid State Properties on Electrode Behavior

The electronic properties of the electrode control the distribution of excess electric charge in the electrical double layer and can also have a decisive influence on the charge transfer reaction at the interface. If the conductivity is metallic, the double layer properties depend more on the crystallographic surface orientation than on the electronic band structure. Semimetals <sup>25</sup> and particularly semiconductors <sup>26,27</sup> have a diffuse space charge layer which is reflected in a very different and asymmetric dependence of the differential capacity on the bias as compared to metallic electrodes.

The difference in band structure is also seen in the charge transfer kinetics. While simple redox reactions on metals depend little on the electron density at the Fermi level <sup>28</sup>, one can distinguish at semiconductors between reactions where electrons of the conduction band are predominantly involved or holes of the valence band <sup>29,30</sup>. At metals, the bias controls the electric field strength in the Helmholtz double layer and affects the height of the activation barrier; at semiconductors the bias controls the concentration of electrons or holes at the surface, and this changes the reaction rate in parallel like the concentration of one of the reactants in a homogeneous reaction <sup>31</sup>. This corresponds to a variation of the entropy factor in kinetics. Surface orientation has a more subtle influence on the charge transfer reaction rates. This is particularly important in multistep charge-transfer reactions at metals in which intermediates being strongly adsorbed on the surface are generated <sup>32</sup>. Such processes are closely related to heterogeneous catalysis in the gas phase (electrocatalysis), and many questions are left open.

### 4. Photoeffects at Electrodes

Light absorption in electrodes generates excited electronic states. If their lifetime is long enough and they can reach the interface, they can induce charge transfer reactions in which the excitation energy diminishes the activation barrier very much or makes the reaction even activationless. In metals the lifetime is very short. The effects are therefore very small. They are equivalent to photoelectron emission into vacuum with three important differences: 1. The barrier height depends on the solvent and can be varied by the bias <sup>33,34</sup>. 2. The reaction yield depends

on the presence of scavengers in the electrolyte that capture the charge carriers irreversibly<sup>35</sup>. 3. Not only excited electrons can be emitted and react with suitable scavengers but also excited holes, i.e., deep-lying vacant electronic states in the conduction band of metals<sup>36</sup>. Such differences should be most attractive for physicists to investigate solid state properties which are not accessible in vacuum<sup>37</sup>.

The reactivity of excited electronic states is much more pronounced at semiconductor electrodes due to their long lifetime therein. This will be dealt with in another contribution to this workshop (see chapter on "The Semiconductor-Electrolyte Interface"). With semiconductor electrodes also the redox reactions of excited molecules of the electrolyte, if they are adsorbed on the surface, can be studied<sup>38,39</sup>. This is connected with the mechanism of spectral sensitization in photography<sup>40</sup>. The result of electronic excitation in solid electrodes can also be luminescence. This has been found at metal electrodes<sup>41</sup> and with much higher quantum yield at semiconductor electrodes<sup>42,43</sup>.

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