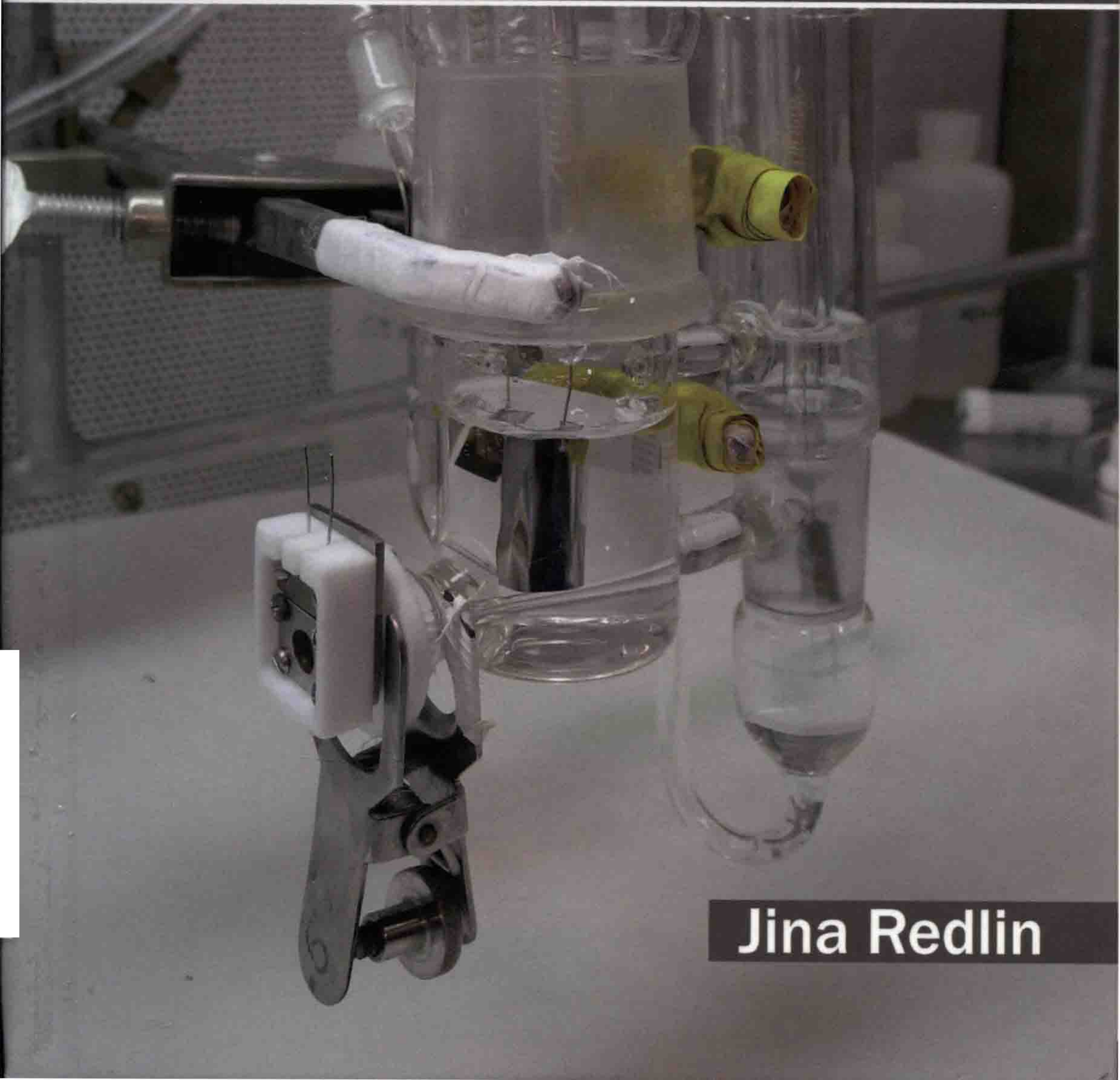
Electrochemical Science and Technology



Jina Redlin

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Edited by **Jina Redlin**

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Preface

This book aims to highlight the current researches and provides a platform to further the scope of innovations in this area. This book is a product of the combined efforts of many researchers and scientists, after going through thorough studies and analysis from different parts of the world. The objective of this book is to provide the readers with the latest information of the field.

Electrochemical science deals with the analysis of chemical reactions occurring at the surface of an electrode. This text presents a selection of topics pertaining to breakthrough procedures applied in the study of electrochemical science and technologies. Elaborations on electrochemical systems along with processing of emerging materials and mechanisms applicable for their operation have been discussed. A detailed account on some of the latest advancements in electrochemical science and technology has been compiled in this book. Special attention has been paid to both the academic and experimental facets of contemporary electrochemistry. The primary emphasis of this book is on the latest progress and accomplishments in the field electrochemical science and technology.

I would like to express my sincere thanks to the authors for their dedicated efforts in the completion of this book. I acknowledge the efforts of the publisher for providing constant support. Lastly, I would like to thank my family for their support in all academic endeavors.

Editor

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Introductory Chapter

Introduction to Electrochemical Science and Technology and Its Development

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1. Introduction

Electrochemistry is a fast emergent scientific research field in both physical and chemical science which integrates various aspects of the classical electrochemical science and engineering, solid-state chemistry and physics, materials science, heterogeneous catalysis, and other areas of physical chemistry. This field also comprises of a variety of practical applications, which includes many types of energy storage devices such as batteries, fuel cells, capacitors and accumulators, various sensors and analytical appliances, electrochemical gas pumps and compressors, electrochromic and memory devices, solid-state electrolyzers and electrocatalytic reactors, synthesis of new materials with novel improved properties, and corrosion protection.

Electrochemistry is a quite old branch of chemistry that studies chemical reactions which take place in a solution at the interface of an electron conductor (a metal or a semiconductor) and an ionic conductor (the electrolyte), and which involve electron transfer between the electrode and the electrolyte or species in solution. The development of electrochemistry began its journey in the sixteenth century. The first fundamental discoveries considered now as the foundation of electrochemistry were made in the nineteenth and first half of the twentieth centuries by M. Faraday, E. Warburg, W. Nernst, W. Schottky, and other eminent scientists. Their pioneering works provided strong background for the rapid development achieved both in the fundamental understanding of the various electrochemical processes and in various applications during the second half of the twentieth century. As for any other research field, the progress in electrochemistry leads both to new horizons and to new challenges. In particular, the increasing demands for higher performance of the electrochemical devices lead to the necessity to develop novel approaches for the nanoscale optimization of materials and interfaces, for analysis and modeling of highly non-ideal systems.

2. Historical background on the development of electrochemistry

2.1 16th to 18th century developments

- In 1785, Charles-Augustin de Coulomb developed the law of electrostatic attraction.

- In 1791, Italian physician and anatomist Luigi Galvani marked the birth of electrochemistry by establishing a bridge between chemical reactions and electricity on his essay "*De Viribus Electricitatis in Motu Musculari Commentarius*" by proposing a "*nerveo-electrical substance*" on biological life forms.
- In 1800, William Nicholson and Johann Wilhelm Ritter succeeded in decomposing water into hydrogen and oxygen by electrolysis. Later, Ritter discovered the process of electroplating.
- In 1827, the German scientist Georg Ohm expressed his law, which is known as "Ohm's law".
- In 1832, Michael Faraday introduced his two laws of electrochemistry, which is commonly known as "Faraday's laws of Electrolysis".
- In 1836, John Daniell invented a primary cell in which hydrogen was eliminated in the generation of the electricity.
- In 1839, William Grove produced the first fuel cell.
- In 1853, Helmholtz introduced the concept of an electrical double layer at the interface between conducting phases. This is known as the capacitance model of electrical double layer at the electrode | electrolyte interface. This capacitance model was later refined by Gouy and Chapman, and Stern and Geary, who suggested the presence of a diffuse layer in the electrolyte due to the accumulation of ions close to the electrode surface. Figure 1 illustrates the Helmholtz double layer model at the electrode | electrolyte interface.

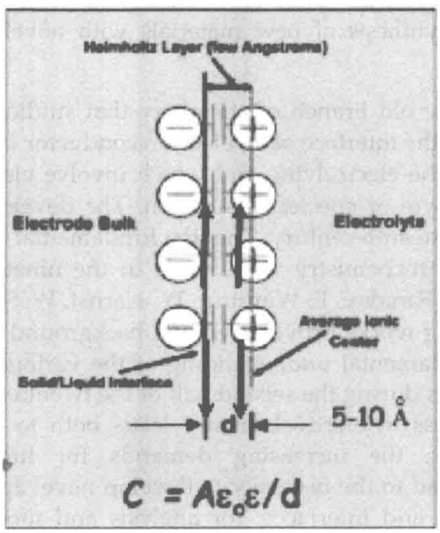

Fig. 1. Schematic diagram of Helmholtz double layer model

- In 1868, Georges Leclanché patented a new cell which eventually became the forerunner to the world's first widely used battery, the zinc carbon cell.
- In 1884, Svante Arrhenius published his thesis on the galvanic conductivity of electrolytes. From his results, he concluded that electrolytes, when dissolved in water,

become to varying degrees split or dissociated into electrically opposite positive and negative ions. He introduced the concept of ionization and classified electrolytes according to the degree of ionization.

- In 1886, Paul Héroult and Charles M. Hall developed an efficient method to obtain aluminium using electrolysis of molten alumina.
- In 1894, Friedrich Ostwald concluded important studies of the conductivity and electrolytic dissociation of organic acids.
- In 1888, Walther Hermann Nernst developed the theory of the electromotive force of the voltaic cell.
- In 1889, he showed how the characteristics of the current produced could be used to calculate the free energy change in the chemical reaction producing the current. He constructed an equation, which is known as Nernst equation, which related the voltage of a cell to its properties.
- In 1898, German scientist, Fritz Haber showed that definite reduction products can result from electrolytic processes by keeping the potential at the cathode constant.

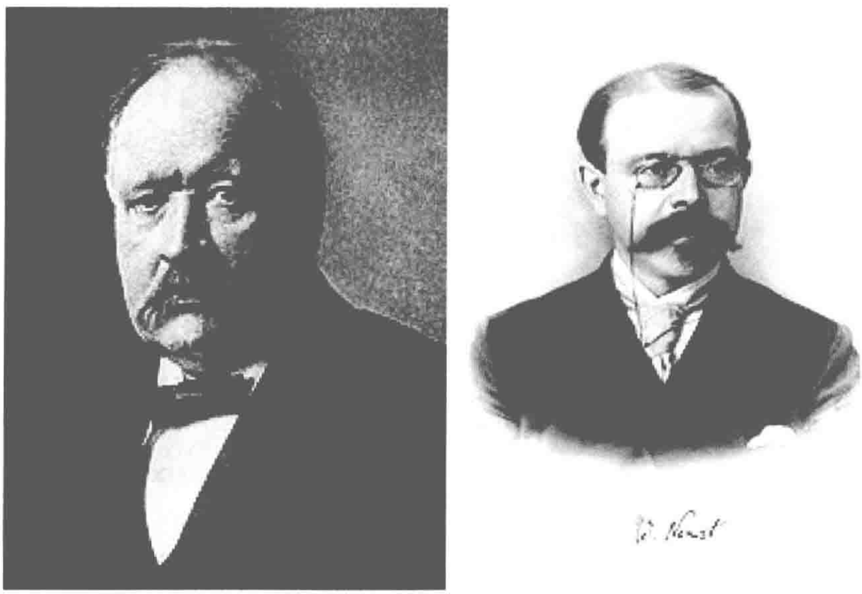

Fig. 2. Pictures of Arrhenius and Nernst

2.2 The 20th century developments

- In 1902, The Electrochemical Society (ECS) of United States of America was founded.
- In 1909, Robert Andrews Millikan began a series of experiments to determine the electric charge carried by a single electron.
- In 1922, Jaroslav Heyrovski invented polarography, a commonly used electroanalytical technique. Later, in 1959, he was awarded Nobel prize for his invention of polarography.
- In 1923, Peter Debye and Erich Huckel proposed a theory to explain the deviation for electrolytic solutions from ideal behaviour.

- In 1923, Johannes Nicolaus Brønsted and Martin Lowry published essentially the same theory about how acids and bases behave.
- In 1937, Arne Tiselius developed the first sophisticated electrophoretic apparatus. Later, in 1948, he was awarded Nobel prize for his pioneering work on the electrophoresis of protein.

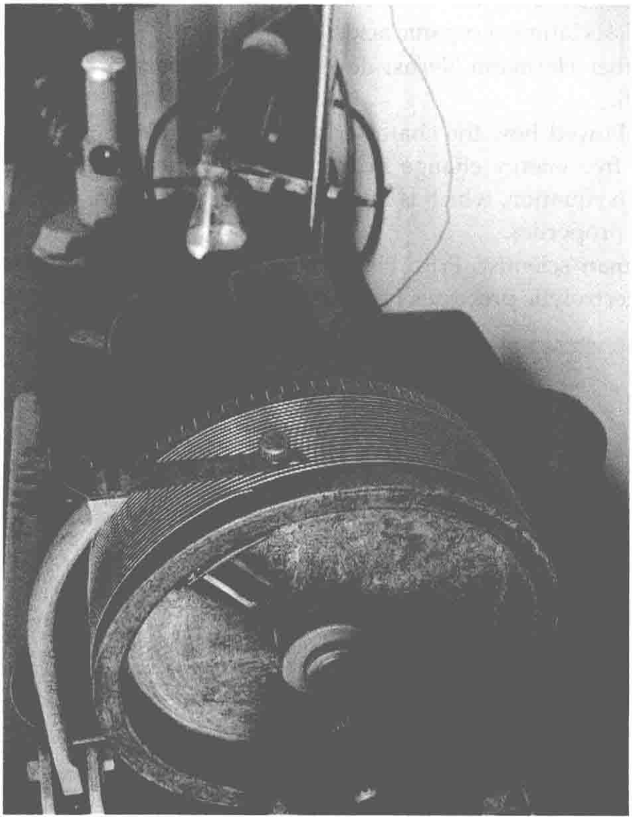

Fig. 4. Heyrovsky's polarography instrument

- In 1949, the International Society of Electrochemistry (ISE) was founded.
- In 1960-1970, Revaz Dogonadze and his co-workers developed quantum electrochemistry.
- In 1957, the first patent based on the concept of electrochemical capacitor (EC) was filed by Becker.
- In 1972, Japanese scientists Akira Fujishima and Kenichi Honda carried out electrochemical photolysis of water at a semiconductor electrode and developed photoelectrochemical (PEC) solar cell.
- In 1974, Fleishmann, Hendra and Mcquillan of University of Southampton, UK introduced surface enhanced Raman scattering (SERS) spectroscopy (Fleishmann et al. 1974). It was accidentally discovered by them when they tried to do Raman with an adsorbate of very high Raman cross section, such as pyridine (Py) on the roughened

silver (Ag) electrode. The initial idea was to generate high surface area on the roughened metal surface. The Raman spectrum obtained was of unexpectedly high quality. They initially explained the intense surface Raman signal of Py due to increased surface area. Later, Jeanmaire and Van Duyne (Jeanmaire & Van Duyne, 1977) from Northwestern University, USA, first realized that surface area is not the main point in the above phenomenon in 1977. Albrecht and Creighton of University of Kent, UK, reported a similar result in the same year (Albrecht & Creighton, 1977). These two groups provided strong evidences to demonstrate that the strong surface Raman signal must be generated by a real enhancement of the Raman scattering efficiency (10^5 to 10^6 enhancement). The effect was later named as surface-enhanced Raman scattering and now, it is an universally accepted surface sensitive technique. Although, the first SERS spectra were obtained from an electrochemical system (Py + roughned Ag electrode), all important reactions on surfaces including electrochemical processes can be studied by SERS.

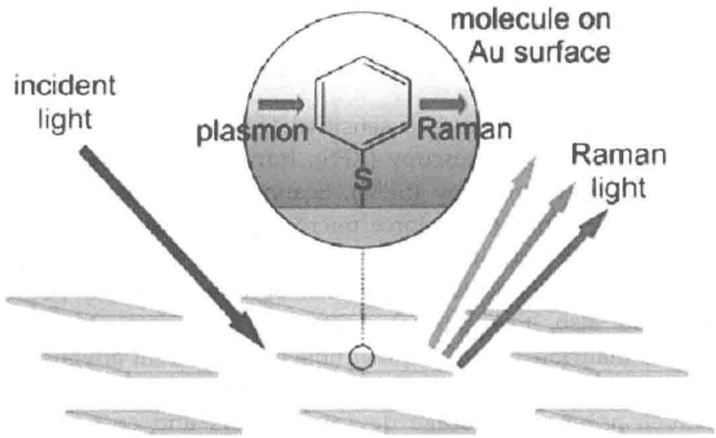

Fig. 5. Schematic diagram to explain the principle of SERS

- In early eighties, Fleischmann and his co-workers at the Southampton Electrochemistry group exploited the versatile properties of microelectrodes in electrochemical studies. The ultramicroelectrodes, due to their extremely small size, have certain unique characteristics which make them ideal for studies involving high resistive media, high speed voltammetry and *in vivo* electrochemistry in biological systems.
- In 1989, A.J.Bard and his group at the University of Texas, Austin, USA developed a new scanning probe technique in electrochemical environment (Bard et al. 1989). This is known as Scanning Electrochemical Microscope (SECM), which is a combination of electrochemical STM and an ultramicroelectrode.

2.3 Recent developments

Development of various electroanalytical techniques such as voltammetry (both linear and cyclic), chrono and pulsed techniques, electrochemical impedance spectroscopy (EIS) as well

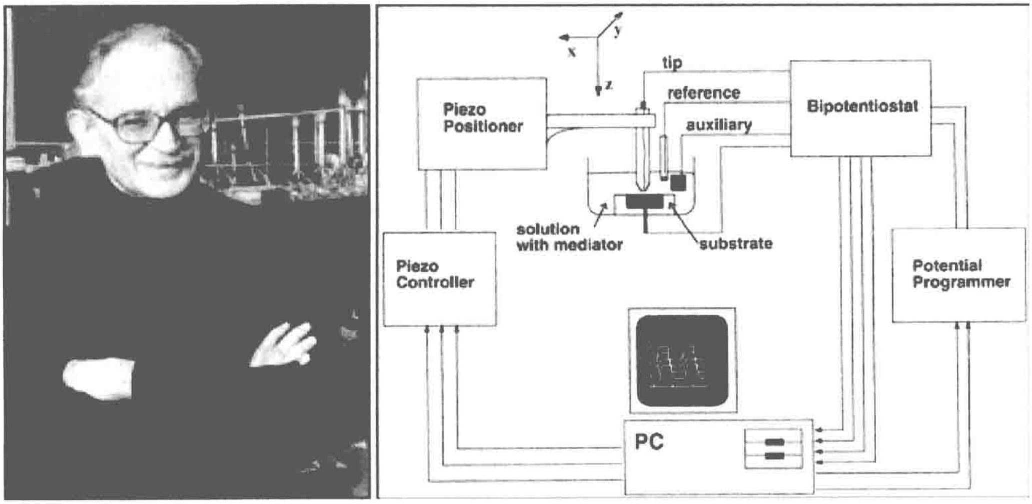

Fig. 6. Picture of A. J. Bard along with the schematic diagram of SECM

as various non-electrochemical surface sensitive techniques such as X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Infrared (IR) and Raman spectroscopy, SERS, Scanning electron microscopy (SEM), Scanning probe techniques like Scanning tunneling microscope (STM), Atomic force microscope (AFM) and SECM has brought a new dimension in the research of electrochemical science and technology. In the recent time, electrochemical science and technology has become extremely popular not only to electrochemists, but also to material scientists, biologists, physicists, engineers, metallurgists, mathematicians, medical practitioners. The recent advancement in material science and nanoscience & nanotechnology has broadened its practical applications in diversed field such as energy storage devices, sensors and corrosion protection. The invention of fullerenes (Kroto et al. 1985) and carbon nanotubes (Iijima, 1991) (In 1980's and 1990's and the recent invention of graphene made a breakthrough in the development of various energy storage devices with enhanced performance. Graphene was discovered in 2004 by Geim and his co-workers (Novoselov et al. 2004), who experimentally demonstrated the preparation of a single layer of graphite with atomic thickness using a technique called micromechanical cleavage. With inherent properties, such as tunable band gap, extraordinary electronic transport properties, excellent thermal conductivity, great mechanical strength, and large surface area, graphene has been explored for diversed applications ranging from electronic devices to electrode materials. The two dimensional honeycomb structure of carbon atoms in graphene along with the high-resolution transmission electron microscopic (TEM) image are shown in Figure 7. Graphene displays unusual properties making it ideal for applications such as microchips, chemical/biosensors, ultracapacitance devices and flexible displays. It is expected that graphene could eventually replace silicon (Si) as the substance for computer chips, offering the prospect of ultra-fast computers/quantum computers operating at terahertz speeds.

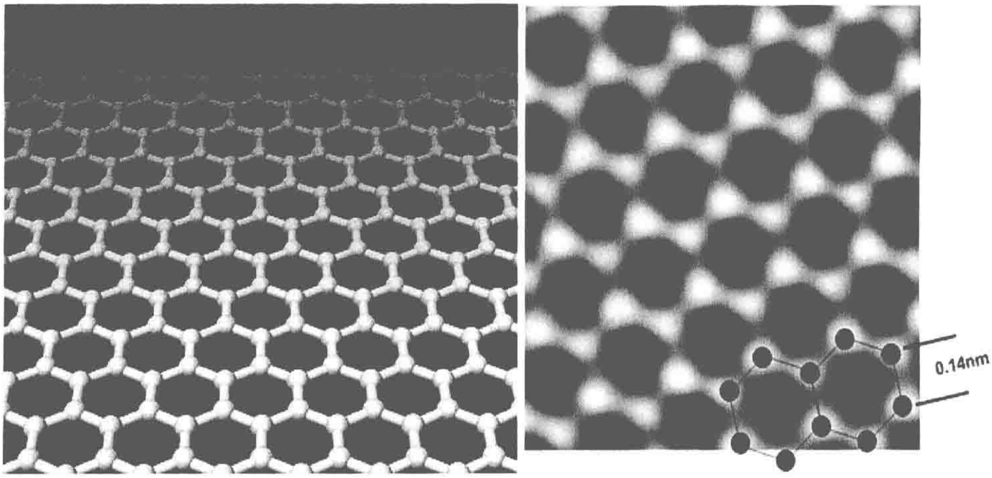

Fig. 7. Two dimensional honeycomb structure of graphene along with the high-resolution TEM image.

3. Conclusion

This book titled "*Recent Trend in Electrochemical Science and Technology*" contains a selection of chapters focused on advanced methods used in the research area of electrochemical science and technologies, description of the electrochemical systems, processing of novel materials and mechanisms relevant for their operation. Since it was impossible to cover the rich diversity of electrochemical techniques and applications in a single issue, emphasis was centered on the recent trends and achievements related to electrochemical science and technology.

4. Acknowledgement

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Part 1

Physical Electrochemistry