

Electrochemistry as a Nanoscience

by O. M. Magnussen

These are exciting times to become an electrochemist. Nanoscience—and to a limited extent even nanotechnology—are here to stay and electrochemistry plays an important part in it. How can we convey this to students, how can we win them as future researchers for this growing field, and how do we prepare them best for upcoming questions and challenges? This is the task faced by electrochemical education today. It is a formidable task and, as I must admit, my own answers to these questions are limited. A key point, however, seems the coalescence of electrochemistry with other areas of surface and interface science, leading (together with other developments in chemistry, condensed matter physics, and materials science) to the current focus on nanoscale structures and phenomena. In the following, I try to sketch these developments and point out some current and expected trends. To facilitate incorporation into practical electrochemical teaching I refer to recent reviews on the field rather than the original literature whenever possible.

The Development of Electrochemical Surface Science

Stimulated by the substantial progress made in studies of surfaces under ultrahigh vacuum conditions, new concepts and techniques started to emerge in interfacial electrochemistry in the 1980s. These rapidly gained ground and have become a vital part of modern electrochemical research. The most important of these developments follow.

Structurally defined electrodes.—Electrodes with well-defined and characterized surface structure are a key component of every electrochemical experiment aiming at an understanding of atomic-scale interface structure and reactivity. Many types of such electrodes, specifically (but not exclusively) low-index and stepped single crystal electrodes of noble and transition metals, can nowadays be prepared routinely with surfaces that are (and stay) clean and smooth on the atomic scale.

In situ methods.—The toolkit of today's electrochemists encompasses a variety of experimental methods for direct *in situ* studies of electrochemical interfaces. Scanning probe microscopy, in particular scanning tunneling (STM),^{1,2} atomic force (AFM),¹ and scanning electrochemical (SECM) microscopy,³ can provide direct real-space images of electrode surfaces with identical resolution as under ultrahigh vacuum (UHV) conditions or data on electrochemical reactivity on the sub-micrometer scale, respectively. Complementary data on the interface structure can be obtained by synchrotron-based methods,^{4,7} such as surface X-ray scattering (SXS),^{4,7} X-ray absorption spectroscopy (EXAFS),^{4,5,7} and X-ray standing wave (XSW),⁷ as well as spectroelectrochemical techniques, *e.g.*, Raman and Fourier transform infrared (FTIR) spectroscopy,^{7,9} second-harmonic generation (SHG),^{7,10} and sum-frequency generation (SFG).¹⁰

Modern theoretical approaches.—Novel insight also comes from studies by advanced theoretical methods,¹¹⁻¹³ ranging from density functional theory (DFT)

calculations of adsorption geometries and energies to molecular dynamics simulations of the double layer structure, quantum chemical models of ion and charge transfer, modeling of phase transitions in adsorbate layers by kinetic Monte Carlo simulations, and description of complex oscillating reactions by nonlinear dynamics.

Together, these experimental and theoretical methods have started to unravel the complex microscopic structure of electrochemical interfaces on the atomic scale. Particularly successful examples are studies of the reconstruction or restructuring of electrode surfaces,¹⁴ of the surprisingly rich potential-dependent phase behavior of adsorbate layers, formed by anions,^{2,15,16} metal species,¹⁷ and organic species,^{2,16} and of the initial stages of metal electrodeposition/dissolution as well as metal passivation.^{17,18} These studies also encompass investigations of the corresponding structural changes on time scales of several seconds to hours.

Contributions of Electrochemistry to Nanotechnology

Over the last decade several developments in electrochemistry have contributed significantly to nanoscience and nanotechnology. Most important are the advances in nanoscale characterization of electrochemical interfaces described above, progress in electrochemical processing methods for the formation of micro- and nanostructures, and the (re-)discovery of electrochemical techniques and concepts by the nanotechnology community, in particular for studying functional nanostructures. More specifically, important current trends include the following.

Nanostructuring by electrodeposition and etching.—Electrochemical deposition and dissolution have proven to be powerful and versatile tools for the formation of structures with lateral dimensions below 100 nm on planar substrates. Examples cover a broad range, ranging from industrial applications, the arguably most important of which is Cu damascene plating for ultralarge scale integrated (ULSI) microchips, to current research, where nanoscale templates (*e.g.*, pores, nanoparticles, natural surface heterogeneities, liquid crystals, and biological or supramolecular structures) are employed to create ordered patterns with dimensions down to a few nanometers. Furthermore, spatiotemporal pattern formation processes in electrochemical reactions can be used to form well-defined multilayers or pore structures (*e.g.*, for photonic crystals).

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Nanostructuring by local probes.—Various schemes for local electrochemical surface restructuring by the tip of a scanning probe microscope have been developed.¹⁹ They employ mechanical interactions between tip and sample (e.g., transfer of electrodeposited material on the tip to the sample or mechanical removal of passivating layers), local changes of the solution composition in the vicinity of the tip (typically induced by an electrochemical reaction at the tip), local double layer charging by a conducting local probe (either by positioning the probe at distances approaching the Debye length or by applying nanosecond pulses), or confinement of the electrolyte to nanosize droplets between tip and sample.

Nanoelectronics.—One key issue in current efforts to construct electronic devices based on single molecules is to characterize and understand electron transfer between molecular species and metal electrodes, a subject which is electrochemistry to the core. Not surprisingly, electrochemical studies therefore play an important role in the development of suitable systems for molecular electronics and are performed by many groups active in this area. (Editor's note: This topic was featured in the spring 2004 issue of *Interface*.)

Nanoparticle synthesis.—Insight into interfacial electrochemistry can also guide the chemical synthesis of nanoparticles by electroless deposition processes. The coverage and structure of anionic and organic adsorbate layers at the open circuit potential may differ for different crystallographic orientations, which in turn can promote selective growth of specific crystal planes. For example, the formation of Au nanorods in cetyltrimethylammonium bromide solution may be interpreted along these lines.²⁰

"Smart" nanomaterials.—Functional nanostructured materials that can be controlled by applying a potential or electric current (e.g., electrochromic layers) or, vice versa, provide electric signals (e.g., sensors based on functionalized electrodes) are particularly easy to integrate into microelectronics and therefore are attractive for many applications. This is already an important area of applied electrochemistry and may be expected to grow in the next few years. Also a wide range of materials for electrochemical energy technology may be added to this category.

This short list can give only a glimpse at the tremendous mutual influence electrochemistry and nanotechnology had on each other in recent years. Many

current trends in this area have been highlighted in past *Interface* issues, which reflect the status of this very active field better than can be given in this brief overview.

Emerging Trends and Future Challenges

Dispite these achievements, major challenges for electrochemical surface and nanoscience still lie ahead, which is good news for students of electrochemistry. Here is a personal view on important contemporary questions and tasks for the next decade(s) of electrochemical research.

Understanding the double layer on the atomic scale.—Contrary to the well-characterized structure of solid metal electrodes and ordered adsorbate layers, experimental data on the local order of the liquid in the near-interface region are sparse and only partly consistent. Likewise, theoretical models are currently not capable of giving a full quantum-chemical description of this complex

interface. A central question is the role of the solvent, in particular water, which can have a decisive influence even on ordered, specifically adsorbed ions in the inner part of the double layer.¹⁵ How the highly dynamic structure of solvent and non-specifically adsorbed ions can be described in detail, in which way it depends on the potential or surface charge density, and how this affects electrode reactions is of key importance to electrochemical surface science. To clarify these issues, advanced *in situ* methods, e.g., ultrafast spectroscopy, as well as complementary *ab initio* theoretical approaches that allow large system calculations and include the electrolyte and the surface charge must be developed.

Dynamics at electrode surfaces.—Atomic-scale dynamic processes on electrode surfaces, such as surface diffusion, interactions between adsorbates, or the initial stages of nucleation, are of considerable importance to a wide variety of

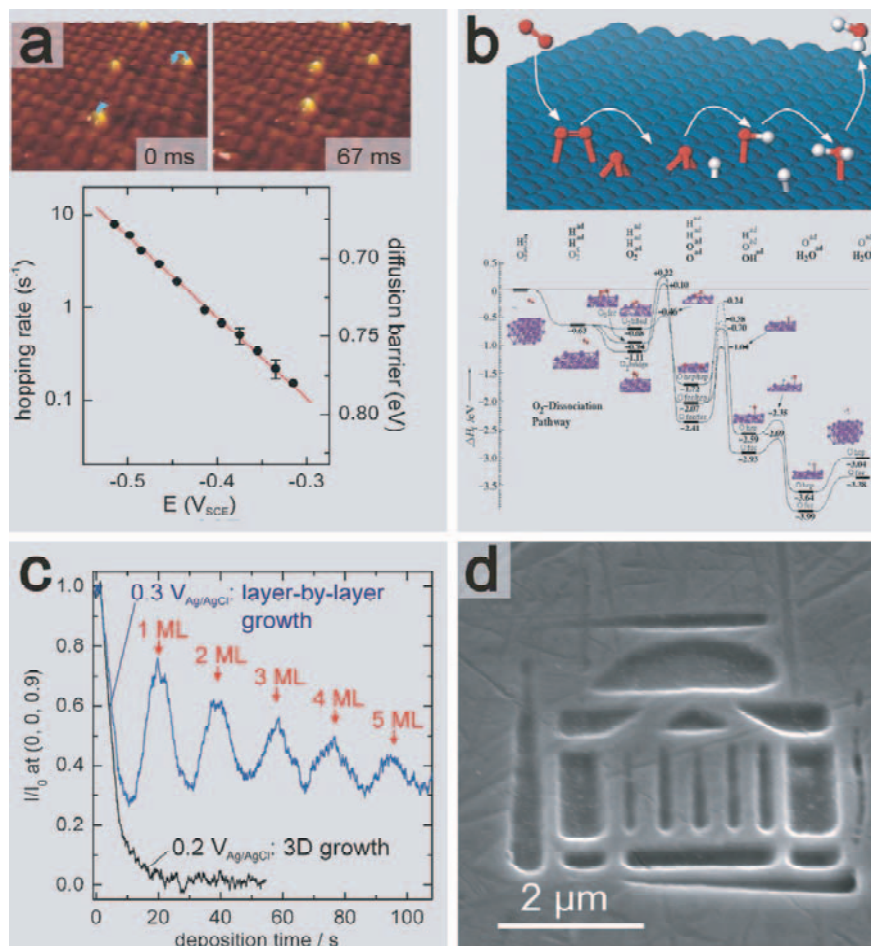


Fig. 1. Examples of current research in nanoscale electrochemistry, illustrating central questions and challenges. (a) Video-STM images of sulfide diffusion on Cu(100) electrodes in 0.01 M HCl solution and resulting potential-dependent diffusion barriers, as an example for *in situ* dynamic studies.²² (b) Clarification of electrocatalytic reaction pathway by DFT calculations for the oxygen reaction on Pt(111) (courtesy of T. Jacob, after Ref. 28). (c) Studies of the interface structure *in situ*, during electrodeposition at deposition rates of $30 \mu\text{A cm}^{-2}$, by surface X-ray diffraction for Au on Au(100), showing the potential-dependent growth behavior.²³ (d) Employing nanosecond voltage pulses for electrochemical machining with nanometer precision (courtesy of R. Schuster, from Ref. 29).

electrochemical reactions, ranging from electrocatalysis to two- or three-dimensional phase formation processes, but are much less understood than their counterparts at solid-vacuum interfaces. Only in recent years, powerful *in situ* methods, *e.g.*, scanning probe microscopy with high time resolution, have become available and have started to unravel the effect of the species in solution and of the high electric field in the double layer on these processes.^{21,22} An example of our own work in this area, a video-STM study of sulfide diffusion on Cu(100) electrodes in HCl solution, is shown in Fig. 1a.²² It reveals a dramatic influence of the potential on the surface diffusion rate, which can be rationalized by electrostatic contributions to the activation energy for sulfide hopping diffusion. Not only the atomic-scale dynamics itself, but also its link to dynamic behavior on mesoscopic and macroscopic length scales is of interest, in particular in the formation of spatiotemporal patterns on electrode surfaces.

Identifying and controlling active sites.—The electrochemical reactivity of the different types of surface sites, present on a real electrode, can differ vastly. Identifying those sites that dominate the electrochemical behavior and ascertaining the microscopic origin of their reactivity is another Holy Grail of surface-science oriented electrochemistry. Although previous studies could determine active sites for selected cases, often revealing a decisive influence of the (potential-dependent) structure of adsorbate layers,¹⁵ a true understanding, based on the full reaction pathway, is still missing for any system. Ultimately, the objective is to describe electrochemical reactivity *ab initio* as a property of the electrode material and the electrochemical environment, linked to electronic structure of the solid surface, the adsorbates in the double layer, and the reacting electroactive species. Obviously, progress in this area is not only of academic interest, but also of great practical importance for the rational design and optimization of electrode materials and electrochemical processing methods. For example, precise knowledge of the mechanisms by which organic additives influence the ion transfer reaction and surface transport of metal adatoms could guide the development of plating baths for nanotechnology applications. Another major area is electrocatalysis (see the example in Fig. 1b), where questions regarding active sites and reaction pathways have been central for a long time and still many open questions regarding the structure-reactivity relationship abound.

Bridging the current density gap.—Similar to the situation in heterogeneous catalysis, where the conditions of model studies differ from those in reactors by a wide pressure gap, electrochemical surface science studies are primarily performed in the double layer regime or at current densities that are several orders of magnitude lower than those employed in corresponding industrial applications, such as galvanic plating. In both cases the interface structure under real-world conditions may be significantly altered by the reaction, *e.g.*, involving the presence of oxides, salt layers, or by-products of the reaction. To develop a technologically useful knowledge, the complex interdependence between atomic-scale surface structure and the electrochemical reaction (*i.e.*, the growth behavior in electroplating) must be clarified *in situ* under realistic reaction conditions, which include high current densities, substantial mass transport in the electrolyte, a wider potential and temperature range, and more complex electrolytes. Attempts to adapt modern *in situ* methods to these requirements are under way (Fig. 1c)²³ and will continue to be an important challenge in the future. A related problem is bridging the materials gap, *i.e.*, advancing to high-resolution *in situ* studies of more complex electrodes (*e.g.*, alloys, nanomaterials) or electrode processes (*e.g.*, polycrystalline or nanoscale-templated growth).

Electrochemistry at short length and time scales.—The breakdown of macroscopic concepts in the nanometer range is the basis of all nanoscience. In the context of electrochemistry this translates to the question of how electrochemical reactivity is changed when the electrode or the electrolyte is confined to nanometer dimensions. This includes, for example, the correlation of structure and reactivity of nanoparticles, a subject of intense research in electrocatalysis. Another, currently largely unexplored example concerns the transport and reactivity of electroactive species in nanoscale cavities, which may offer exciting new science, according to the results from structural biology on transport through ion and water channels. Furthermore, the continuing miniaturization of ultramicroelectrodes opens up new time scales for electrochemical studies. Inversely, ultrafast current pulses are offering new opportunities for electrochemical machining on the nanoscale (Fig. 1d).

Technological applications of electrochemical nanoscience.—Although an impressive range of electrochemical processes for nanostructure formation have been demonstrated already, only a few of them have made it out of the laboratory. Many practical problems,

viz., reliability, long-term stability, and compatibility with existing production methods, must be addressed, specifically for methods based on nanoscale templates or self-ordering.

Required Skills and Implementation in Education

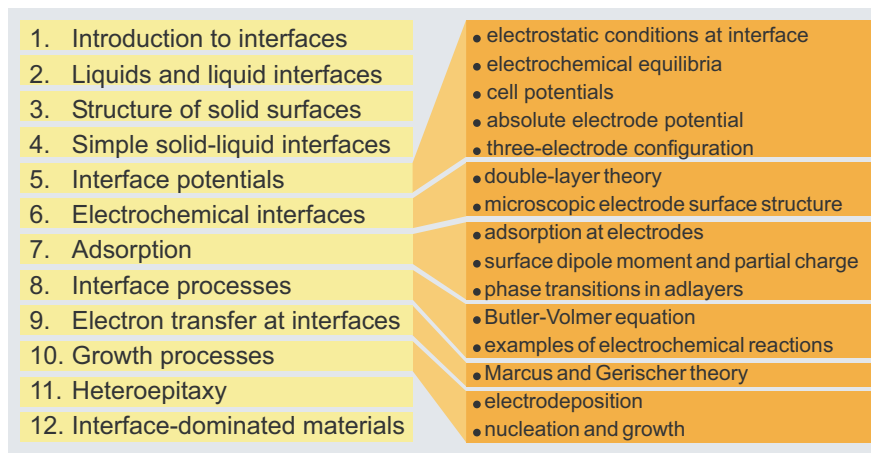
All these areas will provide ample opportunities for basic and applied science, *i.e.*, jobs for scientists trained in electrochemistry. To prepare students adequately for these upcoming challenges is the task of modern electrochemical education, which brings us back to the main issue at hand. The question of how this will (or should) affect electrochemical education is a highly subjective one, depending on the teacher as well as the audience. My own perspective is affected by having spent and taught the last ten years at institutes of physical chemistry and condensed matter physics. Electrochemical education for students with different backgrounds may place the emphasis on slightly different aspects. However, in conversations with colleagues that, like me, have started teaching interfacial electrochemistry in the last few years, the following points were unanimously viewed as central.

Solid working knowledge of quintessential electrochemical concepts.—Above all, our teaching must provide expertise in the core areas of electrochemistry, specifically in charge transfer processes at interfaces. Basic knowledge on how to describe and measure electrode kinetics, *i.e.*, the traditional electrochemical curriculum, is and will remain an essential prerequisite for future contributions of electrochemistry to nanoscience, despite the current emphasis on structural, microscopic issues. However, due to these links to nanoscience, electrochemistry is not exclusively the domain of physical and analytical chemists anymore, but also becomes relevant to condensed matter physicists and material scientists. This has some important consequences.

First, the change in audience must be reflected in the way we motivate and didactically approach these core topics, *i.e.*, the classical lore has to be “reinterpreted.” For example, in my experience, students of solid-state physics usually find electrochemical redox reactions uninteresting, but may willingly embrace lectures on this topic, *i.e.*, on electron transfer between solids and molecules, if they can recognize the connection to molecular electronics.

Second, electrochemical education should not be confined to its traditional place in introductory courses on physical or analytical chemistry anymore. The

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knowledge on electrochemical interfaces and processes. For example, scanning probe microscopy images may illustrate the surface defect structure of solid electrodes, the structure and phase behavior of adsorbate layers, as well as growth and dissolution processes (Fig. 3). In a similar way, data from surface diffraction studies and computer simulations can visualize double layer structure or vibration spectroscopy and DFT calculations may be employed to explain adsorption geometry and elemental steps in electrocatalytic reactions (see Fig. 1b). According to my experience, students find such a visualization or, even better, direct experience with such methods, e.g., within a lab course, much more stimulating and easy to remember than an abstract representation by schematic models. Including modern instrumentation into electrochemical education also strengthens the links to other areas of interface and nanoscience, which share these methods to a substantial amount, and does not involve substantial additional time, in particular in a general interface science course (as outlined in Fig. 2).

Many ideas discussed here are not new, but have already entered the curriculum of electrochemical education. This is also reflected in current textbooks for undergraduate and graduate students that often contain chapters on modern concepts and techniques^{24,25} or are even largely based on those.²⁶ Apart from electrochemical knowledge, the interdisciplinary character of modern electrochemical research demands of young scientists a large variety of skills from other disciplines, such as solid-state and theoretical physics, as well as computer science. This is obvious for modern theoretical studies, but also true

Fig. 2. Integration of electrochemical topics in a course on interface science for third year physics majors. About one-half of the lectures are based predominantly or to a significant extent on interfacial electrochemistry.

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current challenge is to include teaching of central electrochemical concepts in programs on nanoscience and nanotechnology, at present emerging in most science departments. This will not come by itself; it is the task of the electrochemical community to ensure that electrochemical knowledge is incorporated into these new courses and ECS should promote and guide such efforts. Within undergraduate education this will hardly exceed some basic ideas, even in a specialized course, which makes it even more important to strive for a modern, accessible presentation that is integrated into the more general conceptual framework of nanoscience. To illustrate these points, my own attempt at this, a course of interface science for (mostly) third year physics students, is outlined in Fig. 2. As shown in the right part of the figure, quintessential electrochemical concepts are embedded in (at least) half of the lectures of this course.

Concepts of surface science and condensed matter physics.—As shown above, basic concepts of surface science and condensed matter physics play a major role in modern interfacial electrochemistry and should be part of every course in this field. Four areas seem to be of particular importance: (i) an introduction into the microscopic structure of solid surfaces should be given, including surface relaxation and reconstruction as well as surface defects; (ii) students should acquire basic knowledge of the electronic structure of solids and solid surfaces, i.e., band structure, electronic excitations, and surface states. These concepts are of general importance for modern theories of adsorption and electron transfer and essential in semiconductor electrochemistry; (iii) the surface science picture of adsorption and adsorbate layers

should be discussed, which involves description of adsorption as a quantum-chemical phenomenon and some glimpses into the complex 2D phase behavior of adsorbates; and (iv) some insights into modern microscopic growth theories should be provided, e.g., on the elemental processes in homoepitaxial nucleation and growth or the role of stress relaxation in heteroepitaxy. The main objective in all these areas is to convey a microscopic, surface-science oriented view of the electrode structure and of interface processes.

Modern experimental and theoretical methods.—Advances in electrochemical surface science are primarily based on the modern experimental and theoretical tools described above. Students must competently assess the information obtainable by these methods, which require acquaintance with the basic principles. Conversely, modern *in situ* or theoretical studies offer attractive possibilities to communicate basic

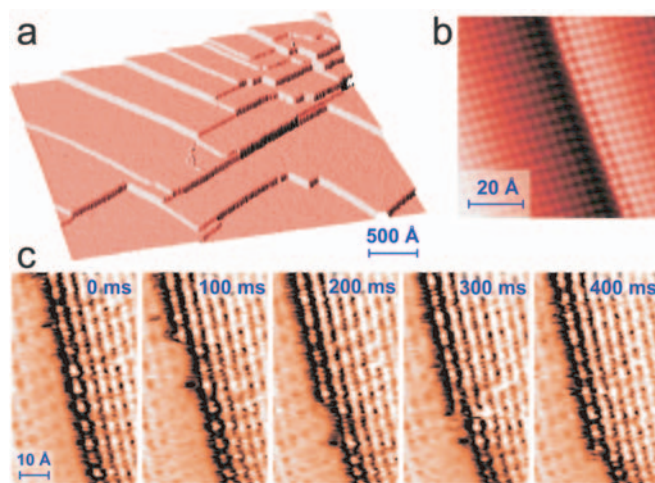


Fig. 3. Visualizing concepts of interfacial electrochemistry using modern *in situ* methods. In situ STM images of Cu(100) in 0.01 M HCl solution; (a) the surface defect structure of solid electrodes, including steps and kinks; (b) the structure of specifically adsorbed adlayers (here a c(2x2) Cl adlayer); and (c) the microscopic growth of the surface via propagation of kinks along Cu steps.

for experimental work. For example, experimental studies on nanoscale surface dynamics, such as shown in Fig. 1a, include the quantitative analysis of large, statistically relevant data sets, which require the development of automated methods for the analysis of high-resolution images. Another skill of considerable relevance for modern experimentalists is some (at least superficial) understanding of electronic circuit design. To impart these skills is far beyond the scope of normal electrochemical teaching. However, electrochemical education must ensure that expertise in these areas can be acquired by students in the wider curriculum of chemistry, physics, or materials science.

Conclusions

The methodical developments of the last two decades helped to establish electrochemistry as a modern, attractive nanoscience. Current interfacial electrochemistry has “cool” toys and “hot” questions, and often offers unique or superior possibilities for nanoscale science and technology. All this should ensure a bright future for this discipline and make it an interesting topic for students coming from diverse areas. To meet the challenges faced in future research, modern electrochemical education must convey a surface science oriented, microscopic picture without sacrificing fundamental knowledge on electrochemical methods and electrode kinetics. Balancing and interconnecting these two sides is a delicate task that, in view of the ongoing rapid development of this field, requires continuous adaptation and depends to some extent on the background and interests of the audience. In the end, electrochemical education can give young scientists only a start on their own journey by providing basic knowledge and, above all, motivating them to ask their own questions and to probe deeper into the complex, but fascinating subject of electrochemical interfaces and processes. The highest that teachers of electrochemistry (or any other science) can hope for is to instill deep curiosity and the sense of wonder and excitement, as described by the “father of nanotechnology.” Richard Feynman: “With more knowledge comes deeper, more wonderful mystery, lurking one to penetrate still. Never concerned that the answer may prove disappointing, but with pleasure and confidence we turn over each new stone to find unimagined strangeness leading on to more wonderful questions and mysteries—certainly a grand adventure!”²⁷

About the Author

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