

# Perspectives on Electrochemical Engineering

by Richard C. Alkire and Thomas W. Chapman

The need for electrochemical engineering arises in society because of technological applications that involve electrochemical phenomena such as synthesis of chemicals, electrowinning and refining of metals, power sources, sensors, surface modification by electrodeposition and etching, separations, and corrosion, to mention a few. Each of these involves components (electrode, electrolyte, separator, etc.) that are tuned in response to prevailing economic variables (such as cost of investment, power, raw materials, product quality) by skillful manipulation of engineering design variables (such as cell materials, cell reactions, current, electrode area, cell voltage, conversion, product quality). The insights needed to tune each component to unique advantage for specific applications are based on a broad range of fundamental principles (thermodynamics, reaction kinetics, double layer and interfacial phenomena, conduction, fluid flow, mass transfer, and current- and potential-distribution phenomena). Electrochemical engineering involves the investigation and use of such fundamental principles as needed to solve practical problems.

Throughout history, the engineering landscape has evolved in response to major societal needs. The invention of the electric generator was followed immediately by development of large-scale industrial electrolytic processes (aluminum, chlor-alkali, electrodeposition, copper refining, etc.).<sup>1</sup> For the better part of a century, these diverse processes had such system-specific peculiarities that they each evolved with their own unique empirical engineering design rules coupled to a unit processes approach.<sup>2</sup> From its first meeting in 1902, The Electrochemical Society played a key role in bringing together industrial practitioners and research scientists. Similarities among different processes were eventually recognized, the most significant being that large-scale processes are invariably driven to a transport-limited rate. For this reason, the engineering research literature of the past half-century has focused strongly on understanding ohmic and mass transport processes, including the effect of hydro-

dynamic flow. One consequence of transport limited behavior, which arises as a result of economic factors, is that the local rate of reaction along an electrode surface can vary from place to place, and thus influence cell performance.

While many contributed, the efforts of Wagner<sup>3</sup> and Levich<sup>4</sup> influenced the emergence of electrochemical engineering, because their work inspired so many others. Several individuals, including Tobias,<sup>5</sup> Ibl,<sup>6</sup> and Hine,<sup>7</sup> established engineering training centers and, with their colleagues, developed important experimental and theoretical methods of study. These efforts led to mathematical analyses<sup>8</sup> that provide a rational basis for engineering design based on continuum equations. However, as Wagner observed forty years ago,<sup>3</sup> molecular engineering “may be important in the future development of industrial electrochemical processes.”

In this presentation, we will trace some of the milestones that have shaped the landscape of electrochemical engineering. For the reasons outlined above, our focus is on transport phenomena with electrochemical surface reactions. Brief retrospectives such as this are by nature incomplete and idiosyncratic, and for this we apologize in advance for the omissions and inadvertent mishaps that characterize individual recollections of past events.

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## Transport Processes

The use of dimensionless ratios to characterize the relative importance of concurrent phenomena is widely practiced in many fields of engineering. Dimensionless ratios also guide scale-over between similar systems. Some of the most widely used ratios have been assigned the names of early users such as Reynolds, Schmidt, Nusselt, Sherwood, etc. In electrochemical applications, where the focus is invariably on balancing transport through the volume with reaction at the surface, the key dimensionless ratio, the polarization parameter that influences the current density distribution in well-stirred cells, was recognized independently by Wagner<sup>3</sup> and by Hoar.<sup>9</sup>

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Many of the more quantitative transport-centric electrochemical engineering analyses<sup>4, 8</sup> can trace their roots to non-electrochemical treatments of transport phenomena,<sup>10</sup> including heat conduction,<sup>11</sup> diffusion and reaction,<sup>12</sup> and convective processes near solid surfaces.<sup>13, 14</sup> By solving transport equations with boundary conditions that describe the kinetics and thermodynamics of surface reactions, one obtains the variation of potential and concentration throughout the electrolyte as well as the rate of reaction along the electrode surface.<sup>15</sup> However, the equations and boundary conditions are fully coupled throughout the volume and surface, so that progress was initially confined to certain limiting cases where the problem could be cleaved into smaller pieces that were more easily addressed.

In the literature through the 1960s, there were three categories of boundary conditions for which the transport equations could be simplified to allow analytical treatment.

**Primary Distribution**—The electrode reaction proceeds readily but at low rates with the result that mass transfer and surface reactions are not important in comparison with ohmic resistance. The potential field is obtained by solving the Laplace equation, and the potential field depends solely upon cell geometry.

**Secondary Distribution**—The electrode reaction is sluggish but proceeds at low rates where mass transfer is facile. The potential field is obtained by solving the Laplace equation with boundary conditions that describe the charge transfer overpotential. The potential field depends on charge transfer resistance, electrolyte conductivity and cell geometry. The “Wagner Number” determines the uniformity of the current distribution along the electrode surface.

**Tertiary Distribution**—The electrode reaction occurs under mass transfer limitations, and the current distribution is determined by the laws of convective diffusion. Two cases were typically explored since they permitted separation of the potential field from the concentration field: (a) binary electrolyte, and (b) excess supporting electrolyte.

During the 1960s, the digital computer came into use for obtaining the current distribution in 1-D porous electrodes<sup>16</sup> and led to a rich variety of treatments that spanned the intermediate regions between the foregoing three limiting cases.<sup>17</sup> In addition, numerical methods were used for analysis of 2-D potential-field<sup>18</sup> problems.

The limiting current method for measuring the electrochemical transport rate played a significant role in the advancement of the engineering field.<sup>19,20</sup> The limiting current is the maximum current that can be generated by a given electrode reaction for a given bulk reactant concentration under steady hydrodynamic conditions. The technique is widely used to establish mass transfer correlations, to measure the local solution velocity, measure diffusivity, analyze for reactant concentration, measure hydrodynamic shear stress, and to characterize the structure of turbulent flow near solid surfaces.<sup>21</sup>

Building on these foundations, the development of increasingly sophisticated mathematical methods using a

combination of analytical and numerical approaches was accomplished in the 1970s.<sup>22</sup> A particularly significant breakthrough that triggered this period was the discovery of how to couple two-dimensional laminar boundary layer transport with two-dimensional potential fields by collapsing both equations into surface integrals which were matched by numerical iteration on a rate equation.<sup>23</sup> The use of this technique for treating the rotating disk electrode was a particularly significant development.

By the 1980s the increase in digital computing power led to broadening of capabilities and to development of finite difference and finite element techniques that have become steadily more sophisticated and more user friendly, moving from the research lab into commercial software that finds wide use for engineering design. In addition, emphasis on improved efficiency of large-scale electrolytic processes and rapid growth in microelectronic applications led

to significant improvements in electrochemical engineering skills associated with multi-phase flow and mass transfer in high rate systems and at irregularly shaped electrodes.

Mathematical modeling of electrochemical systems at the continuum level has advanced steadily over a period of four decades. A wide variety of phenomena can be included with the result that models are widely used for sorting out competing effects, resolving experimental data, articulating scientific hypotheses of mechanism, measuring system parameters, and predicting behavior. Such models provide a rational basis for engineering design, optimization, and control. Generally, however, they are based on empirical characterization of the interfacial processes that appear as boundary conditions in the transport analyses.

### Reaction Processes at Surfaces

While the foregoing events were taking place, concurrent research efforts at the surface had, by the 1990s, moved down to the molecular scale where they are now leading to new discoveries, devices and process inventions. These advances are driving the engineering community today in the need to develop multi-scale simulation tools that bridge both continuum and non-continuum phenomena.

The early literature on primary potential distribution phenomena employed the simplest possible boundary condition: the potential was a constant on an electrode surface. Most analyses of the secondary potential distribution used linear or Tafel approximations for the surface reaction rate. Tertiary phenomena at the mass-transfer-limiting current used the condition that the reactant concentration was a constant (zero). Increased complexity in description of surface reaction processes grew rapidly in the 1960s when improved control of experimental conditions was achieved through use of potentiostatic power supplies.<sup>24</sup>

The distribution of current density along an electrode surface, which usually varies from place to place, can be measured directly by segmenting the test electrode and measuring the current to each while holding all segments at the same potential.<sup>25</sup> The technique was first implemented by recognizing the

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value of elementary reactions (especially the ferricyanide and acid copper sulfate systems) that gave highly reproducible results, and was greatly enhanced by developments in electronic circuitry, especially operational amplifiers.

Quantitative advances in the area of coupled transport/reaction phenomena, such as AC-impedance spectroscopy, came initially from the electroanalytical area and from 1-D porous electrode applications, and later with the rotating disk electrode and also microelectrodes for fast reactions. Such developments addressed double layer and adsorption phenomena as well as coupled heterogeneous and homogeneous reactions on metal and semiconductor electrodes. These events facilitated discoveries such as conducting polymers, chemically modified surfaces, sub-monolayer surface films, passive oxide layers, adsorbed inhibitors, surface salt films, and others. The situation also led to rapid improvement in understanding of corrosion processes.<sup>26</sup>

Still more powerful experimental methods continued to be developed for control and direct observation, including high vacuum and ultra-clean surface preparations, surface spectroscopy, and scanning methods for obtaining local information.<sup>27</sup> These methods paved the way for several decades by probing the electrochemical interface at unprecedented levels of resolution, thus shifting the focus of electrochemical science to small spatial scales ranging from the wavelength of light down to the molecular scale. These events are leading to discoveries and new technological applications where control of events at the small scale is critical to product quality. Noteworthy among all such techniques has been the invention and rapid development of scanning tunneling and atomic force microscopies for the observation of electrochemical surfaces. The methods are by now generating images of such high quality and quantitative precision as to be stimulating new theoretical efforts in understanding non-continuum molecular phenomena at the fundamental level.<sup>28, 29</sup>

Although simple electrode reactions may be yielding to molecular-scale theoretical analysis, characterization of multiple simultaneous reactions still requires empirical and indirect methods. Such situations are important in the deposition of alloys or composites, in complex reaction mechanisms, in efficacy of additives, and in processes with low current efficiency.

### Implications for the Future

Over the decades, engineers have moved into many research areas that were initially explored by chemists and physicists, such as catalysis, polymers, fluid mechanics, and transport phenomena, as well as numerous areas of electrochemistry. Looking toward the future, it is reasonable to anticipate that the same pattern will now occur at the molec-

ular scale. Engineers are already developing new applications in many promising fields. Because the role of the electrical potential is ubiquitous at the small scale, the electrochemical engineering community has a natural position of advantage in such endeavors.

There are many opportunities. Nanotechnology will be increasingly used to synthesize novel materials including functional materials (membranes and separators), hard materials (catalysts), and soft materials (additives and chemically modified surface films). By assembling nanostructured composites (involving semiconductors, conducting polymers, redox mediators, etc.) we will learn to manipulate pores with significant double-layer regions in order to achieve unique properties. Engineering methods for exploiting double layer properties should grow in response to applications that use control at small scales such as in electrophoretic and osmotic flows, microfluidics in MEMS, and colloidal and interfacial phenomena. The role of the potential is central to biological processes (nerves, sensing, membrane transport, cell fusion, etc.) and technological applications will grow as engineers merge qualitative biological insights with quantitative engineering methods of analysis, many of which have been developed in electrochemical applications during the past half century. In the area of sustainability, many topics can be recognized in the environmental area as well as in the greening of

the chemical process industry (such as room temperature ionic liquids for non-volatile solvents).

To pursue such opportunities, it will be necessary to be vigorous in the development of "molecular engineering" for electrochemical technologies.<sup>3</sup> We need well-characterized systems for developing quantitative understanding and predictive tools at the small scale where non-continuum phenomena prevail.

The continued develop-

ing of *ab initio* computational methods will be fundamentally important, but their use in engineering systems that involve the charged solid-liquid interface will provide major challenges for a decade or more. In the meantime, we need accurate parameters to characterize molecular behavior. Obtaining parameters for engineering analysis requires direct nanoscale observations of electrode reactions in various systems, as well as data at different levels in the same system. Improved experimental methodologies are needed for controlling the interface in order to obtain high quality reproducible data, which are essential for engineering characterization of system behavior. The development of predictive tools for engineering analysis of non-continuum interfacial systems will open the door to linking with continuum macroscopic simulations. What used to be called "boundary conditions" will in the future be called something like "the nanoscale region," a boundary layer within a boundary layer.

Many disciplines of science and engineering will be involved in academic and industrial settings and in a global

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context. It is essential to take strategic advantage of information technology. Improved methods for discovery and innovation by scientists and engineers need to follow the early successes of e-commerce and the entertainment industry. Collaborative environments are needed for linking codes, data, and computing resources for use by scientists and engineers. Experimentalists will use tools for deep analysis of data libraries to extract parameter-estimation sensitivities and to resolve competing hypotheses. Modelers will make their efforts easier to use by others with approaches such as object-oriented codes so that many can participate in testing scientific hypotheses, parameters and engineering assumptions. Legacy codes will become more accessible for design and synthesis. Multi-scale simulations will become routine once metadata schemas are developed to link continuum codes with non-continuum codes. Security, authentication, authorization and other measures will need to improve in order to protect intellectual property associated with commercial applications.

Continued emphasis on education in the electrochemical field is essential as many new players in many disciplines will require access to the electrochemical engineering approach to inject molecular-scale understanding into electrochemical systems, devices, and processes in a quantitative, systematic way. The overarching lesson is that systems CAN be analyzed. Scientific hypotheses and mythical explanations need to be tested. Engineers need to develop and then use handholds for testing preliminary ideas before investing major efforts in analysis. Industrial investments in nanotechnology require the trust and confidence that comes with well-engineered, high quality products. Knowledge of the classical strategies pursued with macroscopic tools during the past half-century offers many insightful examples of how to proceed in the future development of "molecular electrochemical engineering." ■

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