The Evolution of Electrochemical Reaction Engineering and Future Directions

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Abstract

Electrochemical phenomena control the existence and movement of charged species in the bulk, as well as across interfaces between, ionic, electronic, semiconductor, photonic, and dielectric materials. The existing technology base of the electrochemical field is massive and of long-standing, dating to the earliest days of chemical process industry. The pervasive occurrence of electrochemical phenomena may also be seen today in nanoscale and biological systems, in microelectronic devices, and in green processes as well as in natural systems. Consider several examples:

• Materials include metals, alloys, ceramics, ionic solids, semiconductors, membranes, coatings, colloids, conducting polymers, and biological materials including proteins and enzymes.

• Phenomena that arise include conduction, potential field effects, electron or ion disorder, electroluminescence, ion exchange, passivity, membrane transport, double layers at boundaries between phases involving free charges, osmotic flow, and electrokinetic phenomena.

• Processes that depend critically on these phenomena include energy storage and conversion, corrosion, membrane separations, electrodeposition, etching, desalination, electrosynthesis of chemicals, refining of metals, and many others.

• Products that result include microelectronic devices, sensors, batteries, fuel cells, coatings, films, metals, gases, chemicals, and ceramics.

During the early yars of the past century, each electrochemical technology was tuned to the economic and technical realities at hand, similarities among many different processes were eventually be recognized, the most significant being that, for economic reasons, large-scale electrolytic processes are invariably driven to a transport-limited rate. Therefore, the electrochemical engineering research literature of the past half century focused strongly on understanding how ohmic and mass transport processes, including the effect of hydrodynamic flow, influence the potential field between electrodes as well as the current distribution, or rate of electrochemical reaction along a surface.

All structural metals are thermodynamically unstable and corrode by virtue of local anodic and cathodic regions that are driven by the energy contained in their local environment. The annual cost of corrosion in the US has been recently estimated to be $276B, or 3.1% of the US Gross Domestic Product. The design principles for corrosion, however, are very different from those used in materials

processing since, when you succeed in corrosion, nothing happens. The key requirement is to understand how failure occurs, and then to design so as to intervene.

Beginning in the 1950's, mathematical modeling of the current and potential distribution in electrochemical systems including corrosion advanced steadily at the continuum level where sophisticated simulations are by now widely used to predict behavior needed for engineering design, scale-up, optimization, and process control. Continuum codes dominate the extensive modeling literature in electrochemical systems. 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 have until only recently been based on empirical characterization of the interfacial processes that appear as boundary conditions in the transport analyses.

During the past several decades, the field has evolved rapidly based primarily on a suite of remarkable new tools that provide the ability to create precisely characterized systems for fundamental study; to monitor behavior at unprecedented levels of sensitivity, atomic resolution, and chemical specificity; and to predict behavior with new theories and improved computational abilities. These capabilities have revolutionized fundamental scientific understanding of interfacial and catalytic processes, as well as contributed to the present rapid pace of discovery of novel materials and devices where product quality is determined at the molecular scale.

To drive new electrochemical discoveries toward technology innovation, new engineering methods are needed in order to ensure product quality at the molecular scale. Recent advances in computer speed and memory, numerical algorithms, and sensor technologies indicate clearly that a systematic approach is possible that integrates scientific knowledge, intuition, experimental data, and simulations. However, today's engineering design tools are based on continuum phenomena and therefore have a blind spot at the molecular scale. In addition, the primary manipulation of operating conditions during manufacturing today occurs at macroscopic length scales. A new generation of science and engineering design methods must emerge to integrate discoveries, concepts, theory, and experimental data with process engineering in order to design and control future multiscale electrochemical systems.

The challenges to building such tools include uncertainties in the physicochemical mechanisms as well as the values of thermodynamic and kinetic parameters, complexities in the simulation of model equations that can span a wide range of time and length scales, lack of manipulated variables and direct measurements of most properties at the nanoscale during processing, and the inapplicability of most existing systems tools to address systems described by noncontinuum and dynamically coupled continuum-noncontinuum models. These challenges specify the requirements for next-generation tools needed for a systematic approach to the design and control of electrochemical systems from molecules to devices.

The ability to use multiscale, multi-phenomena numerical simulations to achieve precise, quantitative understanding at new levels of magnitude, sophistication, and completeness offers a challenge for electrochemical engineering which, when met, will bring enormous benefits through rapid innovation as well as improvements in existing technological applications.