25 Years of Scanning Electrochemical Microscopy

by David E. Cliffel and Robert L. Calhoun

Life is full of unintended consequences. The birth of scanning electrochemical microscopy (SECM) in 1989 is just such a story. In the late 1980s, after Binning and Rohrer published their work on the scanning tunneling microscope (STM)[1] followed quickly by the atomic force microscope (AFM), Professor Allen J. Bard and co-workers at the University of Texas at Austin undertook building their own new scanning probe microscope for direct electrochemical investigations of the electrode-electrolyte solution interface. Building on the spread of ultramicroelectrodes,[2] by insulating the sides of the STM probe tip, Bard and co-workers demonstrated that communication between the tip and substrate could still occur at close distances by the use of an electrochemical mediator. Their first article coining the phrase "scanning electrochemical microscopy" (SECM) was published in 1989.[3] Subsequent articles that quickly followed this seminal work explored the underlying principles,[4] instrumentation,[5] instrument construction,[6] and aspects of SECM. Within a few years, other groups built their own instruments[7] and began to couple different techniques with SECM.[8]

Early applications were basic electrochemical studies like reaction schemes[9] and electron transfer kinetic studies.[10] More exotic efforts came quickly, with the first use of biological samples occurring in 1990,[11] leading later to "humid air" imaging of individual antibodies.[12] Analytically, the first single molecule detection using electrochemistry was achieved by positive feedback at a SECM tip, bringing electrochemistry up to the ultimate level in detection limit.[13] These highlights reinforce the growth in interest in SECM — A Web of Science search shows an increase in papers from about 30 per year in the early 1990s to over 100 per year since 2008.

Regular improvements in SECM technology included improved methods of independently measuring tip-substrate separation, the scaling down from ultramicroelectrodes to nanoscale tip probes, and combination of various instrumentation with SECM including quartz crystal microbalances (SECM-QCM), electrogenerated chemiluminescence (SECM-ECL), atomic force microscopy (SECM-AFM), and scanning photoelectrochemical microscopy (SPECM). Eventually, commercial vendors developed multiple SECM instruments, each with their own unique capabilities and features, which enabled the general electrochemical community to use SECM in a wide variety of applications.

This issue of *Interface* highlights some current representative work being done by very diverse groups expanding on the use of scanning probe microscopies to electrochemical imaging. This includes work using SECM to study nanoparticle electrocatalysts via multifunctional probes by Sánchez-Sánchez and co-workers, the development of scanning ion conductance microscopy by Baker and co-workers, advancements in the use of improved electrochemical atomic force microscopy by Kalinin and co-workers, and finally the use of scanning tips at the junction of electrochemistry and electron microscopy. These developing methods each add a new aspect to the study of electrochemical interfaces using scanning probe microscopy, and each hold a similar promise for the future in understanding fundamental processes in analytical electrochemistry, much in the same way that SECM held for advancements 25 years ago.

Our intent in this issue is to introduce a brief review of these methods to the broader electrochemical community in hopes that present and future scientists and engineers can expand the use of these outstanding analytical tools, and contribute to the continued growth of scanning probe microscopy as a key methodology for advancing fundamental electrochemical knowledge over the next 25 years.

About the Authors

David E. Cliffel earned a BS in Chemistry and Bachelor of Electrical Engineering at the University of Dayton in 1992. He received his PhD from the University of Texas at Austin in 1998 under the direction of Professor Allen J. Bard, and subsequently did post-doctoral work with Professor Royce Murray at UNC-CH. In 2000, he started as an assistant professor of Chemistry at Vanderbilt University (Nashville, TN). He was promoted to Associate Professor in 2007 and recently promoted to Professor of Chemistry. His current research concentrates on the electrochemistry and analytical chemistry of nanoparticles and photosynthetic proteins, and his group has invented the multianalyte microphysiometer for metabolic profiling and toxicology. He may be reached at d.cliffel@vanderbilt.edu.

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