

# Microelectrodes for voltammetry—a personal historical perspective

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**Abstract** Since the 1950s, the field of electrochemistry has undergone rejuvenation numerous times, attributed to such developments as the three-electrode potentiostat, the integrated circuit operational amplifier, surface modified electrodes, computer-based instrumentation, (ultra)microelectrodes, scanning microelectrode techniques, nanostructured materials, and powerful computational packages (such as COMSOL Multiphysics) that facilitate solution of complex diffusion problems. My own career has spanned nearly all of these renaissances in electrochemistry, but for this discourse, I select the development of microelectrodes as an example of how serendipity can alter the direction of one's research career. This is not a complete historical account of the development of microelectrodes but rather a

personal perspective focusing on my own group's contributions to this area.

**Keywords** Composite electrodes · Microelectrodes · Microelectrode arrays and ensembles · Voltammetry

## Introduction

I am honored to have been invited to write about my own personal perspective on the development of the field of electrochemistry for this special issue of *The Journal of Solid State Electrochemistry*, particularly in view of the impressive list of contributors to this special issue. Let me begin by giving a brief summary of my educational background and the forces that directed me into chemistry and electrochemistry. I have had an interest in science since I can remember, with a particular fondness for astronomy, chemistry, and electronics. I went through a number of Gilbert chemistry sets, collected star charts and memorized constellations, and built various electronic gizmos, from simple crystal radio sets to more complex transmitters and receivers for radio control model airplanes (a hobby I still enjoy to this day). My interest in electronics undoubtedly was influenced by my father who owned an electronics repair business (mostly radio and television repair) and passed along to me various pieces of electronic equipment (voltmeters, oscilloscopes, tube and transistor testers, etc.) for which he no longer had use. It was this influence that ultimately led to my love of the interface between electronics and chemistry, i.e., electrochemistry.

As with many of you who have chosen chemistry as a career, I was greatly influenced by a high school chemistry teacher. In my case, his name was Herman W. Lautenbach of Bellefontaine (Ohio) High School, whom some considered to be a cranky German but who taught me to think

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critically and review experimental results with a degree of skepticism. For some reason, he adopted me as his after-hour student and spent considerable extra time outside of class designing and discussing experiments and special projects. He passed away in 1990 and I deeply regret that I did not take the time to look him up after I left high school and tell him how much I appreciated what he did for me. To those of you who still have such an opportunity, I implore you to take the time to thank those who have influenced you and your career.

I obtained both the B.Sc. (1964) and Ph.D. (1968) degrees at The Ohio State University. My Ph.D. adviser was Professor Daniel L. Leussing, who taught me precision potentiometric measurements for studying the equilibrium and kinetics of aqueous solution reactions. Any success I have had in my own career is due in large part to his mentoring, advice, and encouragement. In fact, he practically insisted that I pursue an academic career, and I ended up turning down several job offers from industry to accept a postdoctoral position at approximately one third the industrial salaries. It was a decision I never regretted.

As an aside, Dan Leussing was a Ph.D. student from Professor Izaak M. Kolthoff's group of the University of Minnesota. Professor Kolthoff is widely considered to be the father of modern analytical chemistry who transformed the field of analytical chemistry from a collection of empirical recipes to a fundamental branch of modern chemistry. Thus, I am an academic grandson of I. M. Kolthoff and my students are academic great-grandsons and great-granddaughters of Professor Kolthoff. I mention this because Professor Kolthoff was certainly one of the great pioneers of the field of electrochemistry in the USA following his immigration from Holland in 1927. I am also indebted to Professors James I. Watters and Justin W. Collat at Ohio State for teaching me aspects of voltammetry (although much of voltammetry at that time was polarography at the dropping mercury electrode!).

The final phase of my formal educational experience was as a National Institutes of Health Postdoctoral Fellow at Cornell University (1968–1970) under the mentorship of Professor Gordon G. Hammes, a renowned physical chemist who utilized various relaxation techniques (pressure-jump, temperature-jump, ultrasonic attenuation) to probe fast biochemical processes. Gordon Hammes had studied as a postdoctoral student under the great Manfred Eigen at the Max Planck Institut, and although my research at this stage was not electrochemistry, I learned new areas of physical chemistry and new techniques and instrumentation that have served me well throughout my career. The lesson here is to be not afraid to venture outside your comfort zone to broaden your experiences and your knowledge base. It can only benefit you further down the road. Gordon Hammes left Cornell in 1988 for the position of Vice Chancellor of Academic Affairs

at University of California at Santa Barbara and then accepted a similar position at Duke University Medical Center in 1991. I attended the retirement symposium and dinner for Professor Hammes held on September 27, 2008 at Duke University. I did not want to miss another opportunity to personally thank someone who played such an important role in my career.

I accepted a position as Assistant Professor of Chemistry at North Dakota State University (NDSU) in 1970 and never left. For the most part, I resisted the temptation to cross over to the dark side (i.e., to administration), preferring instead to pursue research and teaching, although I did serve a term as Chemistry Department Chair and later as Co-Director of the NDSU Corrosion/Coatings Research Center. One of the attributes of NDSU that led me to remain there was the equal importance placed on teaching and research, and both carried equal weight when it came to tenure and promotion time. Over the course of my career, I have sensed that the majority of truly outstanding academic researchers also enjoy teaching and are (for the most part) terrific in the classroom. Indeed, teaching and research in the academic environment are intimately intertwined, and I encourage those of you early in your career to find that balance of effort that leads to success and enjoyment of both. As much as I value any success I have had at research, I also value the fact that I have consistently been one of the top-rated teachers in the departments I have served. I can honestly say I do not know which I enjoy more, teaching or research. I think that is a good thing.

Most academic researchers would likely agree that the direction of their research over time is driven by a combination of interest (and/or curiosity) and the availability of funding to support their research program. But often serendipity plays a role, as will be discussed in the next section of this discourse. My own research career can be divided into four major phases, each funded by different federal agencies. The first phase was funded by the National Institutes of Health to probe fast solution reactions of biological interest utilizing stopped-flow and temperature-jump relaxation techniques. The second phase, somewhat overlapping with the first, was funded primarily by the Environmental Protection Agency (EPA), the goal being to assess the impact of coal strip mining on groundwater chemistry in North Dakota, Montana, and Wyoming. It was during this phase that our story on microelectrodes begins, as detailed in the next section. As an aside, it was also during this phase that we developed an interesting approach for measuring the redox potential of a ground water system based on the ability to speciate As(III) and As(V), a method subsequently adopted by the US Geological Survey for use in certain states [1]. The third phase, funded by the National Science Foundation, explored experimental and theoretical transient behavior at microelectrodes of various geometries, discussed in greater detail in the final section of this discourse. The fourth and most

recent phase of my research, initially funded by the Office of Naval Research (1992–1996) and subsequently by the Air Force Office of Scientific Research (1996–2010), involved corrosion and corrosion control of Fe and Al alloys. Much of this work has been in collaboration with my friend and colleague Professor Gordon P. Bierwagen, a physical coatings chemist in the Department of Coatings and Polymeric Materials (CPM) at NDSU. Although not discussed here, this recent research makes extensive use of various scanning microelectrode techniques (e.g., the scanning vibrating electrode technique, local electrochemical impedance spectroscopy, scanning electrochemical microscopy, scanning ion-selective microelectrode techniques, etc.) to probe corrosion mechanisms. Since microelectrodes have been involved in one way or another throughout much of my research career, it is only fitting that I choose to elaborate on our contributions in this area.

### Composite electrodes—the role of serendipity

As part of the EPA-funded research on the impact of coal strip mining on groundwater chemistry, we were interested in the possible release of heavy metals into the groundwater environment from fly ash, the fine particles captured from chimneys of coal-fired power plants. This ash containing heavy metals was to be buried back into the strip mine during reclamation, and the important question was whether the metals remained locked up in the ash matrix or were released as water infiltrated through the material. We used both atomic spectroscopy and anodic stripping voltammetry (ASV) for heavy metal determinations, preferring mercury “thin film” electrodes to mercury drop electrodes for ASV. During the early stages of this work, glassy carbon was available but suffered from being very hard and brittle with electrochemical behavior that was dependent on surface preparation as well as its source. Consequently, porous forms of graphite such as spectrographic graphite rods were commonly used for voltammetry, including ASV. Of course, electrode porosity for voltammetry is generally not a good thing, so the pores in the graphite were sealed using wax or molten paraffin, forming a so-called wax impregnated graphite (or WIG) electrode. Such electrodes had been in use since the mid-1950s and were prone to failure as the wax crystallized and/or cracked, resulting in increased porosity which, in turn, led to broadening of stripping peaks. The lifetime of a WIG electrode in acidic solutions was particularly short, as short as a few hours.

Growing weary of using WIG electrodes for ASV, Jeff Anderson (a particularly enterprising graduate student in my group) decided to explore alternative electrode materials for ASV. Jeff, currently Professor and Chair of Chemistry at Murray State University in Kentucky, developed a composite of finely divided graphite and epoxy

which cured into a solid-state version of a carbon paste electrode, an electrode we termed the “graphoxy” electrode [2]. Containing ca. 50% graphite by weight, this electrode performed very well for ASV in aqueous solution, but an even less reactive binder than epoxy would be desirable for performing voltammetry in organic solvents, such as for flow stream detection for HPLC.

Jeff then turned to the very inert binder polychlorotrifluoroethylene (marketed as Kel-F by 3M Company), long used by chemists because of its inertness in a wide range of solvents, including concentrated alkalis and strong acids. Kel-F is more rigid than its close relative polytetrafluoroethylene (or Teflon) and has less tendency to cold flow, making it easier to polish and to machine into practically any shape, with a working temperature range of  $-200$  to  $+200$  C. These early electrodes were fabricated by blending Kel-F 81 particles donated by 3M with graphite particles (UCP-1-M) obtained from Ultra Carbon Corporation. This is where serendipity played a role in altering the future direction of our research. Various sizes of Kel-F particles were used in the fabrication process (obtained by sieving), but these particles were always much larger (typically  $50$ – $100$   $\mu\text{m}$  in size) than the conductor particles (e.g., graphite, ca.  $1$   $\mu\text{m}$  in size). An analogy would be marbles (the Kel-F particles) and sand (the graphite particles), where a blended mixture of the two would result in the sand filling the interstitial spaces between the marbles, a phenomenon we termed forced segregation of the conductor particles [3]. As a result, when the blend was compression molded, a reticulated network of conductor formed throughout the Kel-F matrix, resulting in good conductivity of the composite even at very low weight percent of conductor ( $<5\%$ ). In fact, too high a conductor load (e.g.,  $50\%$  as used with the graphoxy electrode) resulted in mechanical instability of the composite. The particle size difference between the Kel-F and conductor particles pushed the percolation threshold for conductivity far below that required for a more homogeneous blend of polymer and conductor [3]. On the surface of these composite electrodes, small regions of conductor were surrounded by larger areas of insulating polymer. We discovered an easy way to make an ensemble of microelectrodes!

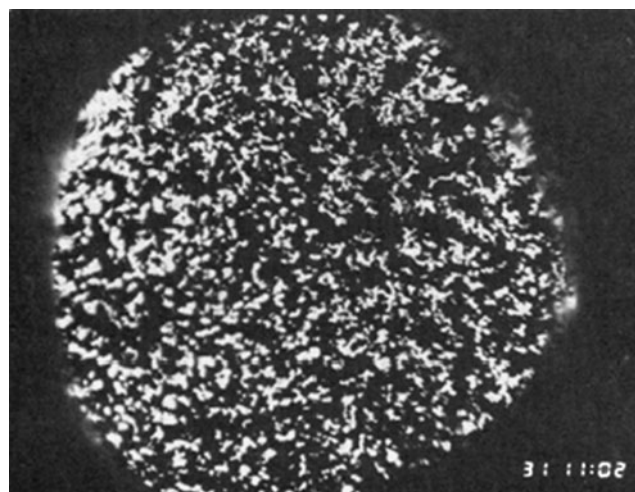
David J. Chesney (currently Professor of Chemistry at Michigan Technological University, Houghton, MI) and Duane E. Weisshaar (currently Professor of Chemistry at Augustana College, Sioux Falls, SD) extended the applications of Kelgraf electrodes to general voltammetry, including electrochemical detection for HPLC [4–9]. It was in this work that we first noticed the appreciable signal-to-noise (S/N) enhancement of these composite electrodes (up to five times) when compared to glassy carbon, particularly when used in channel-type electrochemical detectors for flow stream analysis. The Kelgraf electrodes appeared to be more immune to flow noise (noise generated due to variations in flow rate during the pumping cycle, especially

at potentials where oxidation of mobile phase components can occur), which we attributed to a smoothing of the current fluctuations due to convergent diffusion to the individual microelectrodes during the low flow rate portion of the cycle [9]. Our hypothesis led Mark Wightman and his group to construct a regular  $5 \times 20$  array of 100 disk electrodes using carbon fibers, each  $5 \mu\text{m}$  in radius and separated from its nearest neighbor by at least 6 fiber diameters to eliminate diffusional overlap between disks [10]. Their channel-type array detector was relatively insensitive to pump fluctuations, confirming our hypothesis.

Another source of S/N enhancement for a flow-by array detector is due to what we called depletion layer recharge. As a plug of electroactive analyte flows over a continuous electrode surface such as glassy carbon, the depletion layer grows (i.e., the convective-diffusion layer thickens) toward the downstream edge of the electrode, resulting in lower current contribution from the downstream portion of the electrode. Now envision breaking that electrode into smaller pieces with insulator separating the pieces, keeping the total active area the same, thus keeping the electrode-area-dependent noise the same (flow noise may actually decrease as discussed above). As the analyte plug flows over this array electrode, the depletion layer undergoes a diffusional replenishing as it flows across the insulating regions of the array, leading to greater contributions to current at the downstream portions of the array. Theoretical computations suggest that with proper design of the array, such current enhancement can be significant [11, 12].

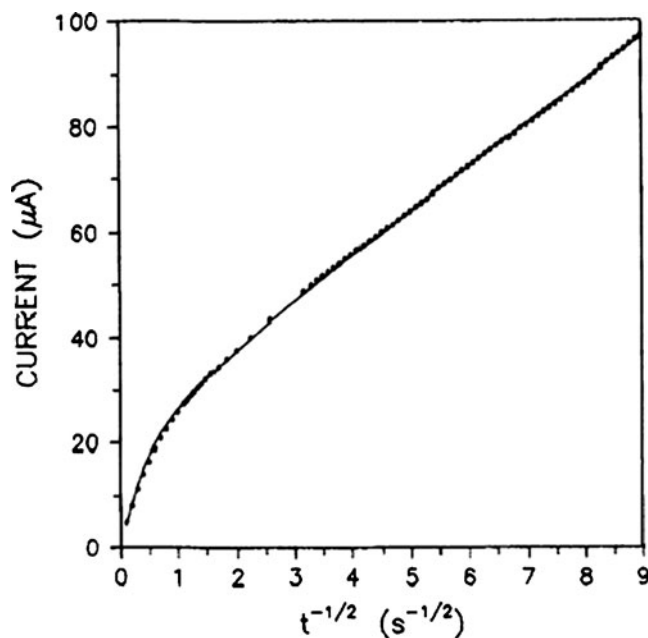
Steven L. Petersen (currently with Pacific Northwest National Laboratory) extended this Kel-F composite electrode approach to other conducting materials, including silver (Kelsil) [13], gold (Kelgold) [14], and platinum (Kelplat) [14]. A convincing illustration that these composites do indeed function as an ensemble of microelectrodes is presented in Fig. 1, where electrogenerated chemiluminescence at a Kelsil electrode is displayed [15]. This experiment was conducted in the laboratory of Professor Royce Engstrom who was then at the University of South Dakota (Royce is currently president of the University of Montana). The observation that the emission boundaries are sharply delineated suggest that the sequence of steps following electron transfer and leading to chemiluminescence is of sufficiently short duration that no luminescence occurs at significant distance from an active region on the electrode surface. Thus, we obtain a map of the active sites on the composite material. Note that many of the active sites (microelectrodes) have a rather high aspect ratio, i.e., a high perimeter-to-area ratio, which further enhances edge (or convergent) diffusion to the site. Imaging of a Kelgold electrode by scanning electrochemical microscopy revealed a similar surface morphology [16].

I conclude this section with an example of chronoamperometric behavior at one of these composite electrodes.



**Fig. 1** Chemiluminescence resulting when the potential of a Kelsil electrode (ca. 3 mm radius) was stepped to  $-1.4 \text{ V}$  vs SCE in the presence of  $0.43 \text{ mM}$  rubrene,  $0.43 \text{ mM}$  benzoyl peroxide, and  $0.1 \text{ M}$  tetraethylammonium perchlorate in DMF. Reproduced with permission of the American Chemical Society from [15]

Figure 2 shows a Cottrell plot for a Kel-F/Au (Kelgold) electrode containing 14% Au by weight over a time range of 10 ms to 100 s [14]. In my (admittedly biased) opinion, this is one of the most beautiful examples illustrating the three regions of microelectrode array behavior. At short times (the right-side linear region of the curve spanning the



**Fig. 2** Cottrell plot of the chronoamperometric response of a 14% Kel-F/Au composite electrode for  $1.00 \text{ mM}$   $\text{Ru}(\text{NH}_3)_6^{3+}$  in  $1.0 \text{ M}$   $\text{KNO}_3$  (buffered with  $0.02 \text{ M}$  phosphate, pH 6.9), with a time range of 10 ms to 100 s. The points are experimental data; the solid lines are theory (least-squares fit). Reproduced with permission of the American Chemical Society from [14]

time range of 10 ms to 100 ms), the microelectrodes behave individually (i.e., no diffusion layer overlap) and the total current follows the equation:

$$i = nFDC \sum_N \left[ \frac{A_j}{(\pi DT)^{1/2}} + \frac{P_j}{2} + \dots \right]$$

$$= nFDC \left[ \frac{A_T}{(\pi DT)^{1/2}} + \frac{P_T}{2} + \dots \right]$$

where  $i$  is the total current density from the ensemble (summed over all  $N$  electrodes in the ensemble),  $A_j$  and  $P_j$  are the active area and perimeter, respectively, of the individual  $j$ th microelectrode, and  $A_T$  and  $P_T$  are the total (collective) active area and perimeter, respectively, of all microelectrodes. The other symbols have their usual electrochemical meanings. The slope of this linear region provides the sum of the areas of the individual microelectrodes, and the nonzero intercept of this linear region provides the collective perimeter of the microelectrodes. Then there is a region of curvature where the diffusion layers of individual microelectrodes begin to overlap. At long times approaching 100 s, the slope of the curve increases, approaching a limit that reflects the entire geometric area of the array (i.e., complete overlap of diffusion layers so that the entire array surface now appears active). Additionally, the curve approaches a zero intercept as for a macroelectrode of millimeter dimension, for which contribution from the perimeter term is negligible.

The solid line in Fig. 2 is a least-squares theoretical fit using an approximate theory developed by Scharifker for an ensemble (random array) of disk microelectrodes that considered overlap of diffusion layers [17] (see [14] for further details). From such a fit (as well as from the short time linear region of the curve), the collective area and collective perimeter of the individual microelectrodes could be determined. The true active area of a Kelgold electrode determined in this way (0.0476 cm<sup>2</sup>) agreed very well with the area estimated from the composite composition (0.0443 cm<sup>2</sup>), and then collective perimeter of the microelectrodes was approximately 80 cm [14]. The perimeter-to-area ( $P/A$ ) ratios of the microelectrodes (e.g., ca. 1,700 cm<sup>-1</sup> for a Kelgold electrode) are equivalent to those of disk microelectrodes with radii of ca. 15 μm.

Observations such as those described above led to our interest in the transient behavior of microelectrodes of well-defined geometry, especially those having high  $P/A$  ratio. Such microelectrodes could be used to develop electrochemical sensors having very high signal-to-noise ratio. A new research direction, attributed to serendipity! Had Jeff Anderson not used Kel-F and graphite particles of such different size in his original Kelgraf electrode, my research might have proceeded in some other direction.

## Transient behavior of microelectrodes

As is probably clear at this point, I am using the term microelectrode to describe an electrode that has at least one dimension on the scale of microns or smaller. Some call such electrodes ultramicroelectrodes, probably to distinguish them from the historical use of the term microelectrode. The three-electrode potentiostat was first described by Hickling in 1942 [18] but was not widely used until the mid to late 1950s. Prior to that time, two-electrode cells were used, usually with a rather massive reference electrode to minimize its polarization when milliamps of current were passed. By comparison, the working electrode was small in size (often millimeter in dimension) and was referred to as the microelectrode. Modern use of the term microelectrode, as recommended by IUPAC, refers to an electrode that has dimensions of tens of micrometers or less, down to the submicrometer range [19]. Alternatively, an operational definition of a microelectrode is “any electrode whose characteristic dimension is, under the given experimental conditions, comparable to or smaller than the diffusion layer thickness,  $\delta$ ” [19]. Either of these definitions suffices for the discussion that follows.

An obvious advantage of a voltammetric microelectrode is its small size that allows it to be placed unobtrusively in very small places, such as in a single cell or in living tissue. Indeed, this was the motivation for the earliest applications of such electrodes, as pioneered by Professor Ralph Adams and his group [20, 21]. At about this same time, Bindra and coworkers described a quasisteady-state method for the monitoring and analysis of current–time transients due to growth of Hg microdroplets on a vitreous carbon electrode, permitting the rate constant for the fast mercurous ion reduction reaction to be determined [22, 23]. Since these early pioneering efforts, the many advantages of microelectrodes and microelectrode arrays (compared to conventional electrodes of millimeter dimension) have been discovered and discussed in the literature, including:

- The small size permits measurements in very small volumes, nanoliter to picoliter or smaller.
- A rapidly attained steady state (or in some cases, a quasisteady state) for a faradaic process, permitting time-independent measurements.
- An improved faradaic-to-charging current ratio, a consequence of charging current decreasing in proportion to electrode area ( $A$ ) while faradaic current decreases in proportion to electrode dimension (e.g.,  $\sqrt{A}$ ). Thus, very short time measurements (e.g., at very rapid potential scan rate) can be made.
- The very small faradaic currents result in a small  $IR$  drop, often permitting use of a two-electrode cell.

- Improved signal-to-noise ratio, a consequence of convergent (or edge) diffusion, particularly for electrodes having high perimeter-to-area ratio or for an array of microelectrodes when the diffusion layers completely overlap.
- When used for measurements in flowing liquids, the amperometric current at a microelectrode array is further enhanced through depletion layer recharge, as discussed in the previous section.

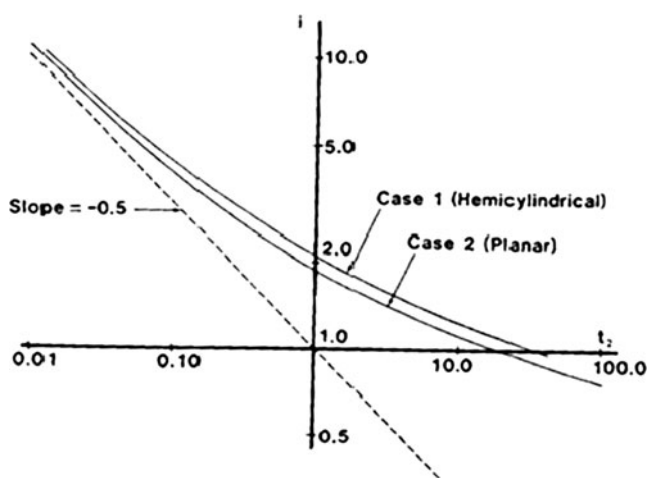
Because of the above advantages, there was intense interest in obtaining a more complete theoretical understanding of microelectrodes of various geometries. In the mid-1980s (when I entered this phase of my research), analytical expressions were available for the limiting short time and long time (e.g., steady state) behavior of the disk microelectrode, as well as finite difference calculations for the disk's complete transient behavior. However, complete and accurate transient behavior was lacking for many other interesting geometries, such as band and ring microelectrodes. The mixed boundary conditions are the key difficulty (e.g., a zero-concentration condition and a zero-flux condition on the same plane containing an embedded disk electrode) and usually rule out analytic approaches, forcing the use of numeric methods instead, the most common being some form of finite difference technique.

Many of the most interesting problems in science are of such complexity these days as to require expertise from different disciplines. One of the smartest decisions I made during my career was to initiate a research collaboration with Professor Davis K. Cope of the NDSU mathematics department, whose specialty is partial differential equations. Davis had performed diffusion calculations for the US Navy earlier in his career, and so we initiated a fruitful collaboration that lasted over a decade. Our initial theoretical work together was designed to understand the depletion layer recharge effect at microelectrode arrays, discussed in the previous section [11, 12]. It was natural to extend our collaboration to better understand transient behavior at individual microelectrodes.

At this stage, we had obtained NSF funding for our collaboration and our objective was to develop a new numerical approach for computing transient current at microelectrodes of high perimeter-to-area ratio, a method that exhibited higher accuracy (on the order of 0.1%) and higher efficiency (could be run on a desktop PC in a few seconds) compared to existing numerical methods. We would then apply this new method to obtain the first complete description of transient behavior at the band microelectrode, a geometry that has one microscopic dimension and one macroscopic dimension, resulting in an electrode which displays microelectrode behavior yet produces conveniently measurable current.

The reader is referred to the original references for details of the method [24–27]. Briefly, it is a hybrid analytical–numerical method consisting of three parts: (1) a Laplace transform with respect to time is applied to the original diffusion equation for concentration. A standard argument converts this “stationary” equation to an integral equation over the electrode surface for the Laplace transform of the flux (this step requires introduction of the appropriate “Neumann function” as the kernel of the integral equation); (2) numerical solution of the integral equation for the Laplace transformed current,  $i(s)$ ; and (3) numerical inversion of  $i(s)$  for the current  $i(t)$ . The efficiency of the method arises since we do not need to compute the entire two- (or three-)dimensional grid for concentration as an intermediate step for obtaining the current. Throughout our work, we referred to this method as the integral equation method, a somewhat generic description. Recently, Mahon and Oldham employed our method for purposes of convolutive modeling and renamed it the Cope–Tallman method [28].

Our first publication on the method with application to the band electrode appeared in 1986 [24]. Figure 3 shows a figure from this paper illustrating the transient behavior for a band electrode over a wide time range. The transient response for a hemicylindrical electrode of equal area is also shown for comparison and as a check of the method (an exact solution for the hemicylindrical case is available from Jaeger's early work on heat transfer). The current and time axes in Fig. 3 are in dimensionless form [24], but for a planar band electrode having a small dimension of  $L=1\ \mu\text{m}$  and for a diffusion coefficient of  $5\times 10^{-6}\ \text{cm}^2/\text{s}$ , the dimensionless time range shown corresponds to a physical time range of  $5\ \mu\text{s}$  to  $50\ \text{ms}$ . If the electrode were a planar



**Fig. 3** Dimensionless current vs dimensionless time for the hemicylinder and planar band electrodes. The scalings correspond to equal area electrodes on the same time scale (see reference for scaling factors). The broken line of slope  $-0.5$  corresponds to Cottrell behavior. Reproduced with permission of Elsevier from [24]

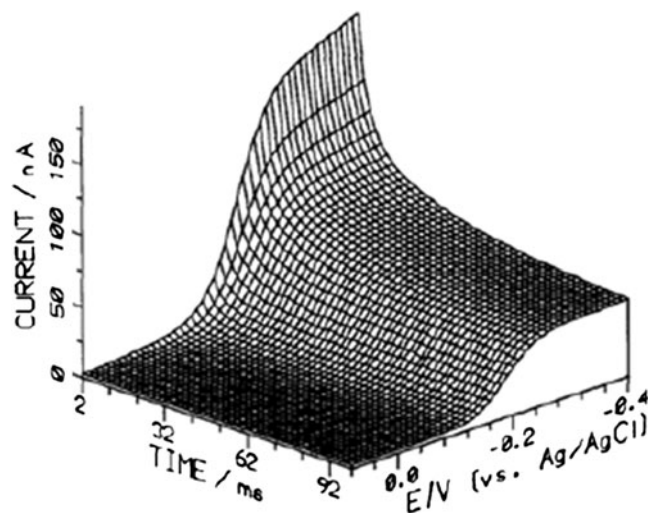
macroelectrode with  $L=1$  mm, the time range would be 5 s to 13.9 h. This was a clear indication that we must modify our perception of “short” and “long” times when dealing with microelectrodes. Note that even at the shortest time shown in the figure, there is substantial departure from Cottrell behavior for electrodes having such high perimeter-to-area ratio. Furthermore, at sufficiently long times, the current at the hemicylindrical electrode is 15% higher than that at a planar band electrode of equal area, independent of time. This suggested that diffusion to the planar band electrode at long times could be described by diffusion to a hemicylinder electrode of somewhat smaller area, a conjecture first proposed by Szabo and subsequently verified (see below) [29].

In January of 1986 (prior to publication of our planar band manuscript referenced above), the US National Science Foundation sponsored the International Conference on Ultramicroelectrodes at Homestead Lodge near Salt Lake City, Utah. The 3-day conference was organized by Stanley Pons and Martin Fleischmann, who (unbeknownst to most of us) were conducting their “cold fusion” experiments at the University of Utah. It was a beautiful setting for a conference, with hot pools available for relaxing and discussing microelectrodes under the mountain skies in the evening after formal sessions ended. All the key people in the field of microelectrodes were in attendance, maybe 40 people if I remember correctly. On Friday evening, Attila Szabo presented a talk on the band electrode. He discussed a conjecture which permitted him to compute the Laplace transform of the current at the band electrode based on behavior at the hemicylinder electrode, but he could not verify the conjecture (i.e., the Laplace domain result) and was unable to obtain the time domain current. He concluded his talk by asking if anyone had further information on transient behavior at the band. In fact, my talk scheduled for the next morning was on that very topic, so the program was reorganized to allow me to present my talk immediately after Szabo’s. I presented my talk, and following that evening session, Szabo, Mark Wightman (who had experimental transient current for a band electrode) and I got together to compare results. Our transient solution for the band electrode gave both the Laplace transform of the current, which confirmed Szabo’s conjecture, and the time domain current, which agreed well with Wightman’s experimental data. While at the meeting, the three of us drafted a manuscript which was subsequently published [29]. It was a fun time to be an electrochemist!

My collaboration with Professor Cope continued several more years, as we extended our method to other electrode geometries [27] (e.g., ring[30–32], disk [33], and tubular band [34]), to various forms of voltammetry (e.g., staircase [35], linear sweep [35, 36] and square wave [37]), and to various conditions of electron transfer [26, 38, 39].

Let me conclude with one final example from our work, namely the generation of a three-dimensional  $i-t-E$  surface at a ring microelectrode, shown in Fig. 4 [40]. The data was generated by a computer-based potentiostat designed in our laboratory that employed digital timers and bidirectional direct memory access techniques to establish the potential and acquire the data (i.e., no software was involved once the experiment started) [40]. The plot consists of 10,000 data points collected from 50 potential step transients, each of 100 ms duration recorded at a different step potential (indicated along the  $E$  axis). A 20-s wait period at the base potential (+0.1 V) between steps permitted reestablishment of bulk solution conditions at the electrode surface. The entire experiment was completed in less than 17 min and the  $i-t-E$  surface embodies virtually all the electrochemical information (thermodynamic and/or dynamic) obtainable from the system under test. Such an experiment would be tedious at a stationary macroelectrode of millimeter dimension since the charging current contribution at short times and the effects of natural convection at long times would render the data questionable, not to mention the long time required to reestablish bulk solution conditions at the electrode surface between steps (although forced convection could be used to reduce this time). Of course, electrochemical systems that lead to electrode fouling would be problematic, although returning to the base potential between steps can lead to regeneration of the electrode surface in some cases.

Although the  $i-t-E$  surface was first discussed in 1960 by Reinmuth [41], Fig. 4 represents, to the best of our knowledge, the first example of such a surface being obtained experimentally in a fully automated manner. As discussed by Reinmuth, intersections of the surface with



**Fig. 4** Current–time–potential surface obtained at a gold ring microelectrode (47  $\mu\text{m}$  outer diameter, 6  $\mu\text{m}$  wide). Solution conditions: 5 mM  $\text{Ru}(\text{NH}_3)_6^{3+}$  in 1.0 M  $\text{KNO}_3$  at 25  $^\circ\text{C}$ . Reproduced with permission of Elsevier from [40]

appropriately oriented planes represent the more conventional (2-D) techniques of normal pulse voltammetry, constant current chronopotentiometry, current sweep chronopotentiometry, potential sweep chronoamperometry (i.e., staircase or linear sweep voltammetry), and potential step chronoamperometry. Typically, we might perform one or more of these 2-D techniques and fit the experimental results with theory, often employing a least-squares approach. As computer hardware continues to become more powerful and computational algorithms (such as the one described here) become more efficient, it is not unreasonable to consider fitting the experimental  $i-t-E$  surface obtained at a microelectrode with a theoretical surface computed from theory. Indeed, this was one direction our research was headed.

## Conclusion

As discussed earlier, our interest in fundamental microelectrode behavior began somewhat by serendipity. Although this phase of my research career was probably the most enjoyable and I still maintain a keen interest in the topic, a new research direction beckoned. Our corrosion program, which started as a side project, was growing in terms of funding and the number of students, to the point that it required my full attention. Our research emphasis changed from fundamental studies of microelectrode behavior to applications of microelectrodes in corrosion research, focusing on such topics as the scanning vibrating electrode technique, local electrochemical impedance spectroscopy, and scanning electrochemical microscopy (SECM). Indeed, we are currently attempting to model SECM probe approach curves to complex Al alloy surfaces using COMSOL Multiphysics, in an effort to determine electron transfer rates at Al alloy heterogeneities. It seems we have come full circle!

I want to end by thanking my students, postdoctoral associates, visiting faculty, and collaborators who have contributed greatly to my research efforts over the years. Whatever success I have had in my career is in large part due to them.

## References

- Cherry JA, Shaikh AU, Tallman DE, Nicholson RV (1979) *J Hydrol* 43:373–392
- Anderson JE, Tallman DE (1976) *Anal Chem* 48:209–212
- Tallman DE, Petersen SL (1990) *Electroanalysis* 2:499–510
- Anderson JE, Tallman DE, Chesney DJ, Anderson JL (1978) *Anal Chem* 50:1051–1056
- Chesney DJ, Anderson JL, Weisshaar DE, Tallman DE (1981) *Anal Chim Acta* 124:321–331
- Chesney DJ, Tallman DE, Peckrul AA, Cook LW, Fleeker JR (1987) *Anal Chim Acta* 197:159–167
- Tallman DE, Weisshaar DE (1983) *J Liq Chromatogr* 6:2157–2172
- Weisshaar DE, Tallman DE (1983) *Anal Chem* 55:1146–1151
- Weisshaar DE, Tallman DE, Anderson JL (1981) *Anal Chem* 53:1809–1813
- Caudill WL, Howell JO, Wightman RM (1982) *Anal Chem* 54:2532–2535
- Cope DK, Tallman DE (1985) *J Electroanal Chem* 188:21–31
- Cope DK, Tallman DE (1986) *J Electroanal Chem* 205:101–123
- Petersen SL, Tallman DE (1988) *Anal Chem* 60:82–86
- Petersen SL, Tallman DE (1990) *Anal Chem* 62:459–465
- Petersen SL, Weisshaar DE, Tallman DE, Schulze RK, Evans JF, DesJarlais SE, Engstrom RC (1988) *Anal Chem* 60:2385–2392
- Wipf DO, Bard AJ, Tallman DE (1993) *Anal Chem* 65:1373–1377
- Scharifker BR (1988) *J Electroanal Chem* 240:61–76
- Hickling A (1942) *Trans Faraday Soc* 38:27–33
- Stulik K, Amatore C, Holub K, Marecek V, Kutner W (2000) *Pure Appl Chem* 72:1483–1492
- Keller R, Mefford I, Oke A, Strope E, Conti J, Wightman RM, Plotsky P, Adams RN (1977) *Mod Pharmacol Toxicol* 10:761–780
- Cheng HY, Schenk J, Huff R, Adams RN (1979) *J Electroanal Chem* 100:23–31
- Bindra P, Brown AP, Fleischmann M, Pletcher D (1975) *J Electroanal Chem* 58:39–50
- Bindra P, Brown AP, Fleischmann M, Pletcher D (1975) *J Electroanal Chem* 58:31–37
- Coen S, Cope DK, Tallman DE (1986) *J Electroanal Chem* 215:29–48
- Cope DK, Scott CH, Kalapathy U, Tallman DE (1990) *J Electroanal Chem* 280:27–35
- Cope DK, Tallman DE (1987) *J Electroanal Chem* 235:97–106
- Cope DK, Tallman DE (1995) *J Electroanal Chem* 396:265–275
- Mahon PJ, Oldham KB (2004) *Electrochim Acta* 49:5041–5048
- Szabo A, Cope DK, Tallman DE, Kovach PM, Wightman RM (1987) *J Electroanal Chem* 217:417–423
- Cope DK, Scott CH, Tallman DE (1990) *J Electroanal Chem* 285:49–69
- Cope DK, Tallman DE (1990) *J Electroanal Chem* 285:85–92
- Kalapathy U, Tallman DE, Cope DK (1990) *J Electroanal Chem* 285:71–77
- Cope DK, Tallman DE (1990) *J Electroanal Chem* 285:79–84
- Engblom SO, Cope DK, Tallman DE (1996) *J Electroanal Chem* 406:23–31
- Kalapathy U, Tallman DE (1992) *Anal Chem* 64:2693–2700
- Kalapathy U, Tallman DE, Hagen S (1992) *J Electroanal Chem* 325:65–81
- Tallman DE (1994) *Anal Chem* 66:557–565
- Cope DK, Tallman DE (1991) *J Electroanal Chem* 303:1–15
- Cope DK, Tallman DE (1994) *J Electroanal Chem* 373:53–59
- Tallman DE, Shepherd G, MacKellar WJ (1990) *J Electroanal Chem* 280:327–340
- Reinmuth WH (1960) *Anal Chem* 32:1509–1512