

Biography and Reminiscences of a 40-Plus Year Career as a Chemistry Faculty Member

Why am I a Chemistry Faculty Member? *Part A.* This was strongly influenced by my father, Royce Leeroy, who was a high-voltage expert and worked for the Alabama Power Company. He had a working shop in the family home, and I learned a great deal about motors and switches, soldering and wiring, machine tools (lathe, drill press), and microscopes and small tools (he repaired watches on the side). So technical things (technical for that time) were ordinary to me. I was inquisitive about how things worked, and this aspect of my personality was fun except the time I messed with an old refrigerator that used SO₂ as a refrigerant and nearly gassed myself!

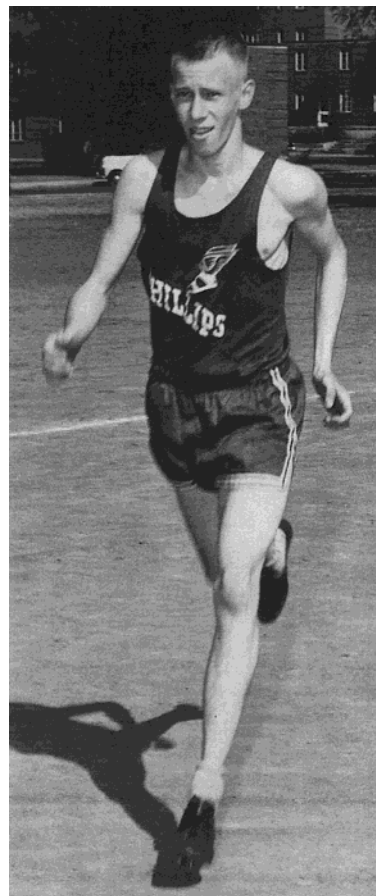
Part B. I had a super Professor at Birmingham Southern College for general chemistry, and I was hooked.

Part C. It was so obvious to me that I wanted to be a Professor at that time that I do not recall ever even struggling with it. I have never for one moment had second thoughts about the decision.

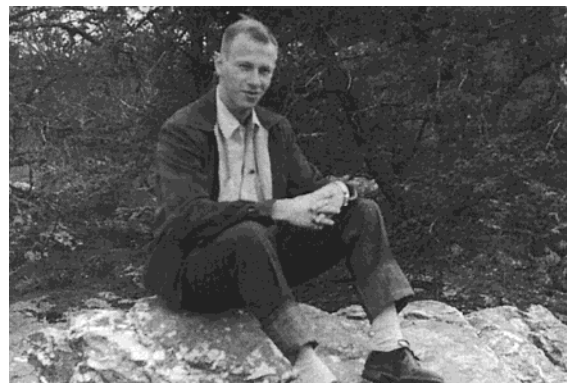
Part D. I had a really good analytical chemistry Professor the next year and enjoyed the quantitative aspects of that kind of lab work, and the mathematical rigor of describing processes such as equilibria and light absorption. So there—I was going to be an analytical chemistry Professor.

How did I get to Graduate School? My father was from east Texas and, as a child, moved with his parents in a covered wagon to southern California, but the family did not like it there and moved back to Eastland County, Texas. He had a high school education and worked in the oil fields, where he learned to rewind burned-out motors and gained a practical experience in electricity. He was a hunter-fisher outdoors man and taught me the craft of fishing as a youngster. My mother only has an elementary school education (but was smart). She and her mother ran a boarding house in the working-class part of Birmingham (“North Birmingham”), and she met my father when he took a room there, coming to Birmingham for a job with Alabama Power. So I was born and grew up in an old but expansive family home. I have one older sister, Amelia, who lives in California. I attended Phillips High School in Birmingham from 1951 to Jan 1954 and, upon graduation, attended Birmingham Southern College, a small liberal arts school, from January 1954 to May 1957, where I graduated with a B.S. in Chemistry, *cum laude*. I also had minors in math and physics. Birmingham Southern had a nice system so that after high school graduation in January 1954, I could squeeze in two quarters in winter/spring; I took summer school in summer 1954, so I got in an entire year of college by fall 1954. I spent the summers of 1956 and 1957 working in labs at a steel plant in Birmingham and at a paper mill in Louisiana. I was not a study nerd in high school or college. In that respect, I was a “normal, rather skinny, tow-headed southern lad”. Neither high school nor college really challenged me in retrospect (although I enjoyed them), so I did not sacrifice grades for sports such as some did. In high school, I played tennis (terribly) and ran distance (state mile champ). In college, I was the intramural sports champ one year.

Grad School at Northwestern. Graduate school was a fabulous experience. I went to Northwestern in the fall of 1957 on the advice of my organic Professor, Ken Gordon (a NU alumnus, naturally). There, I was challenged and learned how



Here (1953), Royce shows us how he learned to be so “fast” in the field of chemistry.



Pondering great things while in college at Birmingham Southern, 1955.

much fun it was to be totally absorbed in chemistry. I learned to study hard and how to keep a focus. I will never forget in my first quarter seeing Howard Zimmerman (now at Wisconsin) teach organic chemistry by writing with the right-hand and erasing (both continuously, it seemed) with the left. Taking notes required focus. I worked with Richard Bowers and Don DeFord and learned electrochemistry and op amps from two masters. My thesis was on designing and building a prototype multi-purpose instrument with lots of Philbrick amplifiers and jack

connections and on studying electrodes covered with membranes ("voltammetric membrane electrodes"). I used Hg as the electrode and various cellulose acetate membranes and reduced metal ions. I learned about finite diffusion, and I learned that the membrane had an ion-exchange capacity that resulted in scavenging of trace metals out of the electrolyte (a nuisance).

I started looking at academic positions in the Fall of 1959 (about six years out of high school) and interviewed at Arkansas, Vanderbilt, and UNC. I had an offer from U. Texas, but they did not even invite me in for an interview, and on the basis of pigs and pokes, I did not buy it. I have often wondered, though, What if Al Bard and I had been on the same faculty...?

Going to UNC, The Southern Part of Heaven. I went to UNC in 1960 (at a salary of \$6000, no startup money at all), and the main reasons were (i) I liked the campus and department and knew that the chemistry department had a solid reputation and, like now, was a congenial place and (ii) Charlie Reilley was there. Charlie was something like a post-doc advisor to me and I learned a lot from him. Charlie taught by asking interminable questions and making you find the answer by asking others. I needed a prodding colleague like him at that tender age. I did not worry about startup money because I needed only supplies to buy electronic components and promptly built a multipurpose op-amp electrochemical system from scratch.

The UNC Chemistry facilities were lousy and crowded, and I was so impressed by that (relative to Northwestern) that I have made a lifetime habit of pushing for new buildings and am currently engaged in planning the 3rd and 4th of my career. I am spending a great deal of time leading the planning for a 493 000 gross square foot "Science Complex" building program—to be completed over the next decade—for the physical sciences (six departments) at UNC; this is something I have worked on for a long time.

I am proud that I have managed to stay at one location my entire career. There was simply nothing that was commanding that enticed me to leave. Besides Charlie Reilley, I have had a host of great colleagues with whom I have interacted, to my immense scientific and personal enjoyment. I would go on to say that the UNC Chemistry culture of respect among the faculty for one another is perhaps over the years our greatest asset because we can work together for common goals that are good for all. And the graduate students have been exceptional. Perhaps my greatest love for Professing is seeing a young student grow in intellectual breadth, forment good experimental design, learn that interpretation is as important as the experiment, and develop a critical attitude. I work graduate students hard, especially the good ones.

"Rotating" at NSF. Another career event that was important to me was a one-year stint at the NSF as a rotator in Analytical Chemistry. (A digression: Fred Findeis was the regular Program Officer and went on a two-year assignment to NSF in Japan. Richard Nicholson (the same as Nicholson and Shain and now the Publisher of *Science*) took the first rotator year (but stayed on after it), and I took the second. So I was the first rotator in the NSF Chemistry Division (who actually rotated).) Spending a year reading proposals was a great learning experience and irreversibly broadened my views of what could be called analytical chemistry. Looking back, the broadening influence turned out to be rather profound, and my lab has published in many chemistry sub-disciplines, with physical chemistry having seen perhaps the most emphasis. Again, my early love for all things quantitative makes that natural for me. An additional influence was to reinforce my proclivity to pursue methodologies that solve chemical questions as opposed to methodology for its own sake.

On Being an ACS Editor. This again, like NSF, has made me learn a lot about fields that I had not personally used in research. My reason for becoming Editor was simple—it was a service to a discipline of chemistry that had been very good to me and had proved to be a fabulous profession. I have met a lot of really bright folks young and old whom I would not otherwise have known and who through their authoring and reviewing efforts display their own love for analytical chemistry. Being Editor has also taught me about how important ethical behavior is in science; I had not previously understood the extent to which Editors wind up being champions and enforcers of ethical behavior by people who publish or review.

Research Philosophy. On research, I am a firm believer in switching areas or emphasis every so often, out of boredom, out of the literature of the field getting crowded and its cutting edge getting dulled, or sometimes just for seizing an opportunity (or one of my students or post-docs seizing it) that is more fascinating. More accurately, one should always be on the lookout for something that is more intriguing and original and less understood than what one is currently doing. I would never survive in a federal grants system that contracts you to actually do everything you propose; I think that important and productive changes should be (and are) accomplished within a grant lifetime. I am also convinced that understanding how to property-design molecules and being willing to try to synthesize them are a gateway to new analytical and physical chemistry experiments. Too many chemists avoid understanding synthesis.

The First Decade of Science at UNC. The first decade of research in Chapel Hill was spent developing electroanalytical methods, studying adsorption on electrodes, and carrying an assortment of chemically oriented electrochemical studies. The adsorption interest was part methods but even more the chemical aspects (mostly metal complexes). One experiment that never got much recognition was a "chiral electrode" in 1965 made by adsorbing different enantiomers that displayed (small) differences in chronopotentiometric behavior for chiral reactants. Looking back, this was my first "modified electrode" that had a deliberate design about it. The methods included optically transparent (minigrid) thin-layer electrodes (1967) done by Bill Heineman, who later exploited the topic admirably in his own career. We took the "OTTLE" experiment to the infrared in 1968 and to semi-infinite diffusion conditions in 1971. A number of metal complex experiments in nonaqueous solvents (Hiller, 1967) taught me some great simplifying aspects of aprotic media.

Modified Electrodes—Monolayers. In 1974, Charlie Reilley and I procured an early model of an XPS spectrometer made by Dupont, and although it was extremely crude by today's standards, it proved to be an enabling workhorse experiment in entering the chemically modified electrode (CME) area. We started metal complex (Untereker, 1975) and some surface chemistry experiments, partially as a test of what we could learn with this thing called XPS (or ESCA, as it was more usually known then). Tin oxide was used in the surface chemistry—we had some fluoride-doped tin oxide films acquired earlier for spectroelectrochemical work. I remember getting, at the beginning of 1975, a lunch-time, long distance call at an electrochemistry Gordon Research Conference from Fred Findeis at NSF, who told me about a new energy-related research initiative at NSF which one could write proposals to. Thanks to the XPS initiative, I had already some preliminary results of surface modification in hand and subsequently wrote a proposal, and it was funded. The proposal was on CMEs and contained a figure/cartoon of all sorts of kinds of surface attachments and what



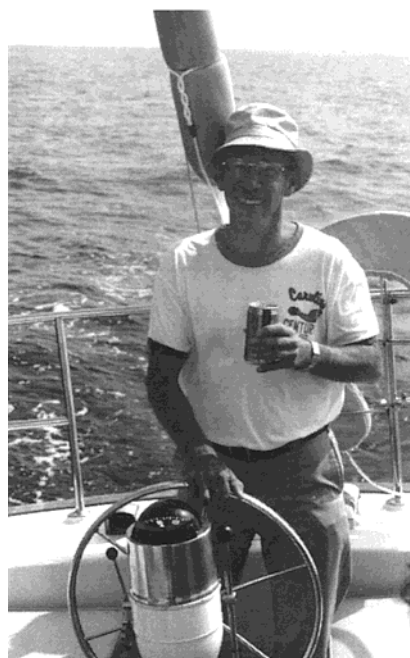
Royce in 1975, while climbing in the U.S. Rockies, ponders whether his group will climb the mountain before them—chemically modified electrodes.

you could do with them. I had a post-doc, Rick (Richard P.) Moses, who had a particularly green thumb in the lab, and a bright Ph.D. student, Larry Wier, and we had our first CME publication later that year (Moses, 1975). Rick went to work for Duracell and Larry at St Bonaventure University.

That was a really thrilling period because (i) we had a tool (XPS) to tell us what we were doing to the surface (Elliott, 1976; Moses, 1976; Untereker, 1977; Moses, 1978; Lennox, 1978). (ii) Also, we successfully explored a series of surface attachment schemes to different electrode surfaces (tin oxide, carbon, RuO_2 (Moses, 1977), and Pt/PtO (Lenhard, 1977)) with silanes and ester and amide coupling reactions. The Pt/PtO surfaces gave the nicest surface voltammetry. Using Pt surfaces, with their native oxide monolayer, was inspired by having read Nick Winograd's XPS study of them. (iii) Finally, we had some synthetic expertise to attach interesting chemicals. My budding collaboration with Tom Meyer was a positive force in the latter sense (Lenhard, 1978; Abruña, 1979). We also inherited a storehouse of functionalized ferrocenes from my colleague Bill Little's research days that was very handy (Lenhard, 1978). The lab studied monolayer CME's intensively until about 1979.

In 1978 (Lenhard), we encountered our first example of voltammetry of multilayer redox films—they sometimes formed on Pt/PtO from organosilane reagents which are very reactive and were prone to form polymers when you did not want them to. These films, while passing charges for their complete electrolysis that were obviously greater than those of a monolayer, were, however, thin enough that diffusion-like electron hopping was not apparent in their voltammetry. It was not until the end of 1979 (Daum; Nowak in 1980), that we encountered, in plasma-polymerized polyvinylferrocene, surface-confined cyclic voltammetry that looked just like a diffusion-controlled CV. I remember having a long discussion in the group about how this could be, and finally, with the help of an insightful publication from a group at IBM and thinking about the experiment of Merz and Bard on poly-vinylferrocene, the light dawned, and we began to understand electron hopping in redox polymers. We wrote an Accounts article in 1980, mainly on the monolayer work that proved to be a magnet for attention to the CME area.

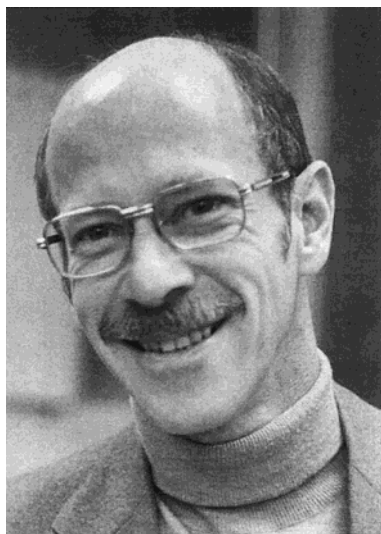
Polymer-Modified Electrodes. The discovery of the electrochemistry of redox polymers changed my lab in about a year, from a focus on monolayers to one on redox polymer films. I was powerless to stop it (even if I had wanted to); the students were instantly interested in polymer film experiments, and they



Full steam ahead, 1980.

were orders of magnitude technically less demanding than the monolayer work was. Yes, doing synthetic reactions on monolayers is tricky chemistry, and there were many experimental failures for "reasons unknown".

In 1981, in collaboration with Meyer and from work spearheaded by a gifted Ph.D. student, Hector ("Tito") Abruña, who was a joint student with Meyer and me, we published our first work on bilayer, rectifying, redox polymer films. Further experiments were published by Denisevich (1982) and Pickup (1984). This was the beginning of my continuing interest in "molecular electronics" as a side bar in my research; one could do electronically interesting things using simple electrochemical principles. This early work (Abruña, 1981; Denisevich, 1982) also introduced the notion of making metal complex polymer films by electropolymerization of ruthenium vinylbipyridines; reduction of the complex to the Ru(I) state actually puts the electron on the bpy ring, making a vinyl-substituted radical anion. One could assemble a $\sim 100\text{-nm}$ -thick film quite readily in this way and, furthermore, manipulate the thickness using simply the time of electropolymerization. Further, electropolymerizing first one metal complex and then another—having a different formal potential—created interfaces between polymer films with well-defined electronic levels. We carried out extensive studies (Daum, 1981; Facci, 1981 and 1982) of the electron-hopping chemistry of redox polymer films; this interest has also had a long time constant in the group. In the early days, the redox polymer films were immersed in a solvent/electrolyte solution, and then in 1985, we moved to films that were dry and bathed in an inert gas. The latter experiment (Jernigan, 1985) was possible because we had learned to make redox polymer films (reductively electropolymerized ruthenium and iron vinylbipyridines and, later (Ellis, 1983), oxidatively polymerized ones and metalloporphyrins (White, 1985; Bettelheim, 1987)) as electrode/polymer/porous electrode sandwiches. They were first used in solutions in four-electrode collector-generator modes (Pickup, 1983), and dry two-electrode experiments were a natural next. An important aspect of them was that the dry metal bpy polymers were ionically conductive at room temperature, so one could (in solvent-electrolyte) electrolytically set the mixed valency of the polymer, remove it



Royce in 1982.

from the solvent, dry it, and then observe thin-layer-like voltammetry. It was through these experiments (Jernigan, 1985), in which the polymer was still ionically conductive, and subsequent low-temperature ones in 1987 (again Jernigan, in which the ionic conductivity was quenched by cooling the sandwiched Ru polymer) that we learned how to drive electron hopping in a mixed valent film by electrical field gradients (without concentration gradients). Studying electron hopping in the same molecular material driven both by concentration and electrical gradients had not been done before, and tying these concepts together so that one could obtain the same rate constant in each approach took some time. Finally, we were satisfied with how to do that in 1989 (Jernigan), with further steps in 1994 (Sullivan).

The progression from wet to dry electrochemistry of redox polymer films in the mid-1980s was accompanied by a number of fun investigations in which we explored, using mostly steady-state voltammetry as RDE or sandwiches, (a) the permeation of other species through the thin metal bpy film (Ikeda in 1982), (b) the ET reactions of other species (mainly at the film/solution boundary), a topic started by Ikeda in 1981—after several other papers Leidner (1984) showed that nominally very fast polymer/solution ET reactions could be studied by choosing the chemistry so that the reaction was thermodynamically uphill and driven by the removal of electrons from the metal poly-bpy film by the electrode—(c) using ion-exchange to incorporate other redox species into films on electrodes (Facci in 1982, following the introduction of the ion-exchange idea by Anson), (d) the change in surface energy (measured by contact angle) when a redox polymer changes charge state (Willman, 1984), and (e) an interesting study by Leidner (1985) that showed that the uphill ET ideas at redox polymer/solution interfaces could be applied to redox polymer/redox polymer interfaces to study the reaction rates between monolayers of contacting, electropolymerized bilayers of redox polymer films. We revisited this experiment in a dry-film format in 1991 (Jernigan).

One of the redox polymer hopping transport papers (Facci, 1982) was a sort of classic experiment on the effect of site concentration on hopping rates (as measured by electron diffusion coefficients). One serious problem with changing concentrations in redox polymers was that concentration changes involved other changes as well, such as extent of cross-linking, counterion concentration, etc. So we developed an isostructural dilution scheme in which the sites in an electropolymerized Os bpy could be replaced with the structurally identical Ru-bpy site. The

results were fascinating, showing a hint of percolation property but a persisting transport rate below the nominal threshold that required a model of short-range site mobility to rationalize.

We studied the transport of metal ions through macrocycle polymer films (Massaux, 1984), thinking that this might be a fruitful hopping topic. Metal complexation was, however, a rather “deep trap” for charge transport at least with that chemistry, and we did not pursue this topic further.

I have done little “conducting polymer” electrochemistry partly because it quickly became a crowded field and partly because I favor being able to know more about the relation of electron hopping events to chemical composition than folks in that field typically know. Burgmayer (1982) published an “ion gate” idea for electrically switching the ion permeability of a membrane, using a polypyrrole membrane deposited on a grid electrode. Wilbourn (1988), in a study of a ladder polymer “BBL”, showed a transition between redox and electronic conductivity in this material as one changed the solvent content of a mixed-valent form.

Feldman (1986) started a brief fling into Prussian Blue electrochemistry based on a desire to measure electron-transfer hopping rates in it. The ensuing series of papers labored under the problems of the poorly behaved stoichiometry of these materials.

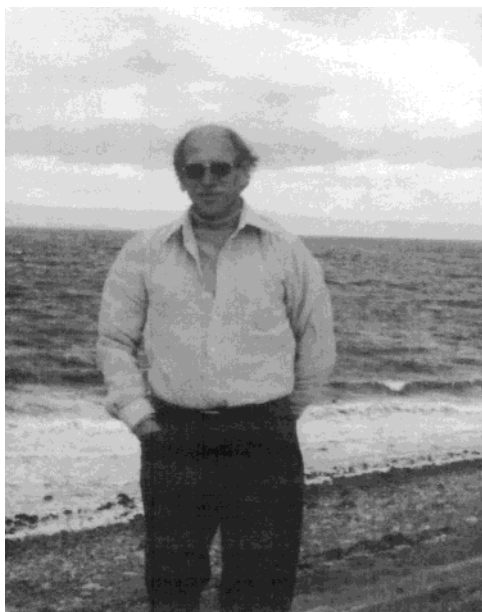
The electropolymerization work with metalloporphyrins and conversations with my former UNC colleague and current fishing pal Jim Collman stimulated some further porphyrin work (Creager, 1985) on high-valent metal states and epoxidation chemistry. This produced in 1986 (Creager, Raybuck) an electrocatalytic biomimetic scheme for Cytochrome P450 epoxidation chemistry and some dioxygen electrocatalysis results (Nishihara, 1990).

In a parallel vein about the same time, in collaboration with Meyer (Kutner, 1985), we looked at high-valent Ru complexes as oxidation electrocatalysts.

Microelectrodes and Polymer-“Tailed” Redox Species.

Having a post-doc named Andy Ewing come to the lab in 1984 was significant in that we learned the techniques of the microelectrode era and entered into it eagerly, first with some polymer film permeation studies (Ewing, 1985) and then with experiments in very low dielectric solvents (toluene and heptane, Geng, 1986), some mediated electrocatalysis of benzene derivatives (Reed, 1986), and porphyrin electrochemistry in toluene (Geng, 1986). The microelectrode applications were interesting, but the previous work with dry redox polymer films (Jernigan, 1985) stimulated our thinking about solid-state electrochemistry in these new media. Reed and Geng (1986) tried some experiments in which the microelectrode, reference, and auxiliary were close together and all coated with a polyethylene oxide film containing an electrolyte and a dissolved redox molecule. These two new directions (the dry redox polymer film voltammetry, and voltammetry in polyethers, which we dubbed “solid-state voltammetry” or SSV) produced changes in the lab’s overall direction, toward semisolid-state electrochemistry and electron transport. The vision was that very little was known about transport and electron hopping chemistry in semisolids (almost no experimental information existed in terms of well-defined, self-exchange reactions).

Reed and Geng, to their credit as bright mid-Ph.D. students, recognized the redox-molecule-dissolved-in-polymer experiments as a significant new direction and dropped their earlier directions. Our initial use of 600 000 MW PEO as the solid-state solvent produced mass transport diffusion coefficients with substantial temperature dependencies caused by melting of the partial crystallinity of the PEO (1986, 1987). We got smart and



Enjoying the Straits of Magellan from the Tierra del Fuego side, 1989.

gravitated toward lower molecular weight polyethers that remain amorphous at RT. The experimental format for SSV was typically a thin film of the polymer solution cast onto a 2–3 mm diameter insulating plane of epoxy containing wire tip electrodes—a microelectrode, Ag reference, and Pt counter. The PEO polymer solution was exposed to a bathing gas, which could be inert or an organic solvent vapor. The latter circumstance allowed exploration of a range of vapor/polymer partitioning experiments (Geng, Reed, and Geng, Longmire, 1989), and we even used the diffusion-plasticizing effect (increased D of the redox solute) of vapor partitioning as a basis for a gas chromatography detector (Parcher, Barbour, 1989). The world did not need another GC detector, but the GC format was very useful for investigation of the plasticization phenomenon in regards to diffusion in polyethers, and a theory was cast for it (Barbour, 1991).

Watanabe (1991) showed that sufficiently concentrated redox species (TCNQ in particular) displayed evidence of electron hopping augmentation of charge diffusion, which opened the door to studies of electron dynamics by measuring diffusion rates in SSV. A limitation on the scope of this topic was the limited solubility of many interesting redox species in polyether solvents (Watanabe, 1990). A cure for this was to attach short poly-ether chains (“tails”) to the redox species; the first version of this was done by Pinkerton (1991). We realized then that the “tail” itself provided an ether-like solvent environment, and we proceeded to investigate the redox polyether hybrids (as we called them) in the pure state (Velázquez, 1993). These materials were much more viscous and exhibited very slow physical diffusion. This finding prompted serious study of ways to use microelectrodes in semisolids with low ionic conductivity and exceedingly slow physical diffusivity. We explored other SSV cell geometries, including lithographically defined arrays of microelectrodes (Morita, 1988), including a “square” microelectrode, interdigitated array electrodes (Nishihara, 1991), the vagaries of microband electrodes (Porat, 1997), and methodologies ranging from considering linear versus radial voltammetric diffusion (Longmire, 1990; Wooster, 1992) to ac voltammetry (Wooster, 1991).

One motivation for the redox polyether hybrids was the avenues they open to semisolid-state electron transfer dynamics, and we successfully measured rate constants in molten salts on the basis of metal complexes with polyether-tailed bipyridine

ligands (Long, 1996 and 1997; Williams, 1997; Emmeneger, 1997; Masui, 1997) and tailed viologens (Hatazawa, 1996; Terrill, 1997) and metalloporphyrins (Long, 1997). Interesting findings included adiabaticity, larger energy barriers compared to monomer redox couples in dilute solutions, and solvent dynamic control of electron-transfer rates (Pyati, 1996; Williams, 1997). We returned to the molecular electronic theme using the concept of frozen concentration gradients (Terrill, 1997) in the metal complex melts to fashion molecular light-emitting diodes from them (Manness, 1996 and 1997). And the concentrated nature of the hybrids meant that, in mixed-valent forms, one could observe optically driven electron-transfer reactions by NIR absorbances (Ritchie, 2000). The differences between the optical and thermal energy barriers are objects of current study.

The lab’s interest in slow diffusion in semisolids also continues, and in this issue of *The Journal of Physical Chemistry B* is found a paper on molecule-scale diffusion, in which voltammetry with diffusion “depletion layers” thinner than the size of a single metal complex is demonstrated and studied. This work (Crooker) is based on redox polyether hybrids of a Co bpy complex. A biological turn was taken in a collaboration with Holden Thorp in devising a room-temperature melt of DNA with tailed metal complex cations (Leone 2000).

Twists and Turns. The preceding story omitted an eclectic array of investigations spanning in the late 1980s and early 1990s: electrochemistry of high-temperature superconductors (HTSC) as electrodes, voltammetry and AFM of very thin electropolymerized insulators, and electron-transfer dynamics of redox enzymes. One investigation was an NSF materials collaborative project (with Marvin Silver—Physics—and Gene Irene—Chemistry) into thin film production and their properties. This work produced new optical probes of the electropolymerized metal complexes (McCarley, 1990) and led into optical, permeation, and AFM studies of thin (nanometer-thick) electropolymerized polyphenol dielectrics (McCarley, 1990 and 1991; Goss, 1992; Brumfield, 1992). The AFM experiments included “nano-dozing” of nanometer-thick polymer films with the AFM tip, an experiment that seems to have been re-invented multiple times. A brief microscopy study of HOPG surfaces revealed some important details about the early stages of their oxidative roughening that included subsurface gas formation, lifting up bubbles of carbon surface (Goss, 1993).

Another foray was into redox enzymes and the question of whether their electron-transfer reaction kinetics would follow the free energy dictates of Marcus theory. In a series of electron-transfer mediation experiments with Co complexes (Corry, 1991 and 1992; Yang, 1993), we found that this was indeed the case for the enzyme sulfite oxidase but not for horseradish peroxidase (Yang, 1994).

The lab broached the topic of electrochemistry at surfaces of high-temperature superconductors in a project led by a postdoctoral fellow John McDevitt and in collaboration with Collman and Little at Stanford. We investigated the substantial corrosivity of HTSCs (McDevitt, 1988; Gollmar, 1989; McDevitt, 1991) and ultrathin microband electrodes and solvents for voltammetry at near liquid nitrogen temperatures (McDevitt, 1989) and reported changes in HTSC electrode capacitance at the T_c onset temperature (Peck, 1992) and voltammetry of ferrocene thiolate SAMs on Ag-coated HTSC at temperatures crossing T_c . The HTSC experiments were accompanied by low-temperature investigations of both solution (Richardson, 1994) and monolayer (Curtin, 1993; Carter, 1995; Richardson, 1995) redox species and descriptions of how to do voltammetry in ultralow-temperature environs.

The low-temperature experiments were among the most technically challenging ones the lab ever had attempted. A side effect was a renewal of interest in chemically modified electrodes in the form of self-assembled monolayers (SAMs). Beyond the low temperature work, this began with investigation of thiolated porphyrins (Hutchison, 1993; Postlethwaite, 1995, 1996, and 1997). The study, among other things, showed that a *cofacial* porphyrin's dioxygen electrocatalytic activity on gold differed from that of the same porphyrin chemisorbed on carbon; i.e., the substrate makes a difference.

Monolayers in 3-D. The tribulations of characterizing porphyrin SAMs lead to a hypothesis that forming monolayers on Au colloids should facilitate their characterization. After some preliminary experiments and following a significant paper by Brust (1994), the lab was on its way to becoming hooked on the chemistry and electrochemistry of nanoparticles and a larger vision of them than characterizing porphyrin SAMs.

The Brust synthesis produces Au nanoparticles in the 1–5 nm diameter range, coated with a dense thiolate monolayer. The monolayer coating was the immediately appealing aspect of the nanoparticle product, allowing it to be isolated, reprecipitated, and dried without aggregation of the metal cores. In other words, these materials can be treated as a new kind of molecule, with a hard core and soft exterior, and invite derivatization with functional groups and linking to surfaces and other materials. We dubbed them monolayer-protected clusters (MPCs) in order to emphasize the protective role. Our first publication on MPCs was a multidimensional (NMR, SAXS, thermal) attack on the analytical chemistry of alkanethiolate-coated MPCs and a study of their solid-state electronic conductivity (Terrill, 1995). Hostetler (1996), Ingram (1997), and Templeton (1998) took key steps in expanding the functional chemistry of the monolayers on these materials, and Wuelfing (1998), Templeton (1999), and Chen (1999) produced MPCs with polyether monolayers, highly polar, water-solubilizing monolayers, and aryl monolayers, respectively. Further analytical studies as a function of alkanethiolate chainlength Hostetler (1996) and core size (Hostetler, 1998) provided additional understanding of MPC structure. Au is not the only metal of interest; Cliffel (2000) and Zamborini (2000) studied MPCs with Ag and Pd cores, and Hostetler (1998) showed that alloy cores could be produced. Likewise, thiolate monolayer-protected MPCs do not require thiols for their production but can be alternatively be made using thiosulfate salts (Shon, 2000). Fluorescent probes attached to MPC cores are substantially quenched but the quenching is quite structurally sensitive, as might be expected for energy transfer quenching by the metal-like core (Aguilla, 2000). MPCs with certain kinds of monolayer ligands are themselves highly luminescent; the relationship of ligand to luminescence is not yet understood (Huang, 2001).

The functionalization chemistry led to attachment of redox species to MPC surfaces and studies of their electrochemistry (Green, 1997 and 1998; Ingram, 1997; Miles, 2001). One-electron couples of redox species on MPCs exhibit more or less normal reactivity at electrodes and similarly normal chemical reactivity when used as mediator-catalysts (Pietron, 1998). The electron equivalents stored on MPC cores can be used for chemical reactions, as demonstrated with a potentiometric titration of a redox substance (Pietron, 1999), and also are preserved when the charged nanoparticles are removed from solution and subsequently redissolved.

A further step into nanoparticle electrochemistry came with a study, in collaboration with Robert Whetten (Ingram, 1997),

of MPC double-layer charging in which the dissolved MPCs had relatively monodisperse Au core sizes. This enabled detection of serial, single-electron charging steps as a fascinating progression of evenly spaced voltammetric peaks. The voltage spacing between the single electron peaks was shown to depend (Chen, 1998) on the MPC core size—developing a molecule-like band gap at the smallest sizes and on the alkanethiolate monolayer chain length (Hicks, 1999). Theories proposing that the single-electron charging should follow a Nernstian relation (Chen, 1998) and that the MPC capacitance can be modeled with a concentric sphere capacitance relation (Hicks 1999) were confirmed. The single-electron, double-layer charging characteristics of MPCs are preserved when they are attached to electrode surfaces as monolayers (Chen, 1999) or as multilayers (Zamborini, 2000).

Single-electron charging properties can be used to characterize MPC cores to charge state and mixed valencies thereof. This allows one to formulate explicit electron-hopping and self-exchange reactions and thereby enables investigation of the rates of electron transfers between MPC cores. The rates are moderated by the monolayer dielectric thickness in a classical exponential (tunneling) manner, as shown for alkanethiolate monolayers and mixed monolayers both in the solid state (Wuelfing, 2000) and as multilayer films attached to electrodes and bathed in electrolyte solution (Hicks 2001).

It has been fascinating and fruitful to develop the chemistry and electrochemistry of MPCs treating them as new kinds of molecules. The end of this story is not yet in sight, but one conclusion can be drawn, which is that nanoparticle research involves such a great diversity of measurements, chemistry, and physical ideas that it is an ideal platform for broadly educating graduate and post-graduate students.

On the Homefront. I married Judy Studinka in 1957, and we have five children (Kathy, Stewart, Debra, Melissa, and Marion). Kathy took her college degree from UNC and lives in Harrisburg, NC and is a high-level Medical Technologist studying for an MBA. Stewart was also a UNC graduate and, after a stint in the Navy flying combat aircraft, now flies for United Airlines and has a home in Amisville, VA. Debra, another UNC graduate, lives in Baton Rouge, LA; after time spent in the Peace Corps in Ecuador, she took up a Ph.D. thesis on tropical butterflies and moths at Louisiana State University. Melissa obtained a B.S. and an M.S. (Ceramics Engineering) at Rensselaer Polytechnic Institute, worked on superconductor materials at GE, and then decided to become a veterinarian, took a degree at Cornell, and practices (large animals) in up-state NY. Marion took her undergraduate B.S. at Penn State and then an M.S. in forestry at Oregon State, and she is now a horticulturist in Portsmouth, RI. I remarried in 1982, to Dr. Mirtha Umaña, who is an author, chemist, and stained glass artist.

Finally, this spring, I received the Thomas Jefferson award here at UNC (it's the top campus award).

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Best Regards,
Royce
June 19, 2001