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13. ABSTRACT ***(Maximum 200 Words)***

Funding from the AFOSR (F49620-94-1-0449) made possible:

(a) to establish that the vectorial and non-linear nature of the redox process provides a switching mechanism that can be used to build matrix-addressable electrochromic displays without cross-talk and with no need for fabrication of non-linear elements -like transistor switches- within each pixel. In contrast, it should be noted that in order to eliminate cross-talk in liquid crystal displays (LCDs) one transistor switch must be incorporated within every picture element (pixel), resulting in high cost;

(b) to develop sol-gel materials with electrochromic properties for light modulation applications, or photoluminescent properties for chemical sensor applications; and,

(c) to investigate and establish that strong, reproducible and quantifiable stirring effects with no moving parts can result when transverse magnetic fields are applied across the current flowing through electrochemical cells. The parameters controlling the magnetohydrodynamic stirring effect have been identified, isolated and studied independently, resulting in an equation that comprises the magnetic field equivalent of the well-known Levich equation for the rotating electrode.

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FINAL REPORT

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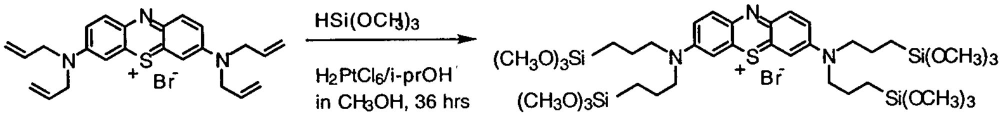
With AFOSR funding we have established a 0.5 μm-resolution fabrication lab within the Chemistry Department of UMR, the first of its kind on this campus. (A glimpse of that lab may be obtained in our departmental home-page at: http://www.chem.umr.edu:80/) We have also purchased electrochemical and time-resolved spectroscopic and imaging equipment, and we have hired graduate students to pursue research on several areas. Our Air Force grant is currently acknowledged in 14 publications, of which 9 are in print, one in the press, one submitted and three to be submitted in the very near future. As more work has been initiated during the AFOSR funding period but is being completed afterwards, it is projected that this AFOSR grant will be referenced by at least another 5 publications. Copies of all publications acknowledging this AFOSR grant, including those submitted or in the press, are attached to this report as an appendix.

(a) Electrochromic Materials and Systems. Electrochromic materials are redox active substances whose different redox states have different color. For certain applications (e.g., for energy efficient electrochromic windows of variable transmittance) it is desirable that the electrochromic materials be polymeric and confined as thin films on the surface of transparent electrodes (e.g., FTO or ITO). In this realm, we developed an electrochromic material (going from colorless to blue upon oxidation) that is able to develop covalent bonding with oxidized electrode surfaces. That material, MB[$Si(OMe)_3$]$_4$ - see eq. 1, is based on the methylene blue chromophore, modified with - $Si(OCH_3)_3$ groups. Along the way we developed and optimized: (1) a new method for the synthesis of the methylene blue ring system, (*Tetrahedron* **1997**, *53*, 10083); and, (2) a new electrochemically assisted polymerization method for the formation of silicate films containing the methylene blue moiety (*Chem. Mater.* **1997**, *9*, 2621-2631). Our electrochemically assisted polymerization method is based on the fact that methylene blue is a cationic dye, while its reduced form (leucomethylene blue) is neutral and therefore precipitates



MB(allyl)$_4$ **MB[Si(OMe)$_3$]$_4$** eq.[1]

on the electrode from neutral aqueous electrolytic solutions; the local high concentration of hydrolyzed -$Si(OH)_3$ groups in the precipitate promotes polymerization and cross linking.

Still dealing with electrochromics, but on a completely different line of work, we have demonstrated and published (*J. Electrochem. Soc.* **1998**, *145(4),* L55-L58) that the vectorial nature of the redox process can be utilized to matrix address two-dimensional arrays of solution-phase electrochromic picture elements (pixels) without cross-talk (see Figure 1). Notice that the pixels adjacent to the ones addressed are not colored at all. To achieve the same effect, liquid crystal displays rely upon either complicated electronic addressing schemes, or on the so-called active-matrix-addressing method. The latter increases the cost of the display panels dramatically as it requires fabrication of one transistor switch within every pixel. It is interesting that in electrochromic displays the switching mechanism that eliminates cross-talk is inherently embedded in the coloration process of the electrochromic materials.

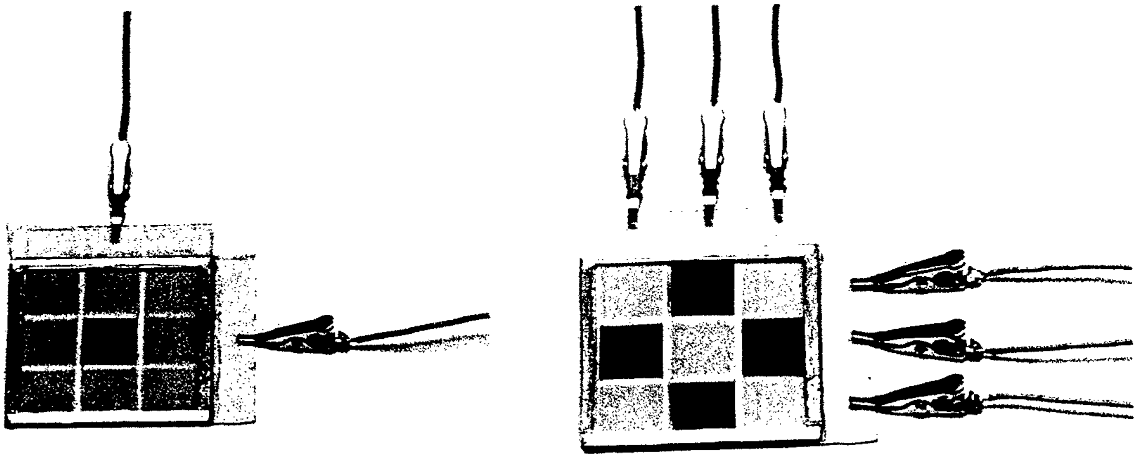
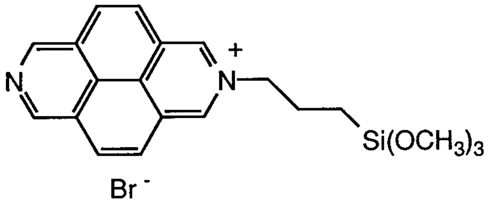


Figure 1. Photographs of a 3x3 array of solution-phase electrochromic pixels based on heptylviologen and *N,N,N′,N′*-tetramethyl-*p*-phenylene diammine (50 mM each). Pixel area 1.57 cm^2; pixel thickness ~190 µm. Left. Steady-state addressing of pixel (2,2) with a 0.5 V bias. Right. Typical matrix addressing: a pattern is displayed by scanning the rows repetitively one-line-at-a-time, while addressing for the columns is reconfigured for every row.

We are planning to expand this work by microfabricating (on the same substrate) a very large number of open-face matrix addressable pixels. We are currently modeling the coloration-decoloration process in order to optimize both the pixel geometry and the chemical composition for fast-switching flat panel electrochromic displays.

(b) Sol-Gel Materials for Sensors. Our work on -$Si(OCH_3)_3$ group modified methylene blue and our electrochemically assisted polymerization method attracted the attention of the scientific community, and I was invited by Dr. Debra Rolison to spend the summer of 1998 at the Naval Research Laboratory in Washington D.C. conducting research on silica aerogel monoliths doped with DAP, a redox-active molecule synthesized at UMR for its luminescent properties, in the spirit of $MB[Si(OMe)_3]_4$.



DAP

Our collaboration with Dr. Rolison led to two methods of doping with DAP: bulk modification and post doping. The latter modifies only a thin skin near the outer geometric surface of the aerogel monolith. The resulting materials are highly photoluminescent (Figure 2), and we found that their photoemission can be quenched by oxygen, opening the possibility for their use as oxygen sensors. In fact, to the best of our knowledge, the speed of the emission quenching is the fastest known for this class of materials. It is limited only by the time required for oxygen to diffuse through the open mesoporosity of the silica aerogel monoliths. As it turns out, gas molecules diffuse through silica aerogel monoliths almost as fast as they diffuse in open air.

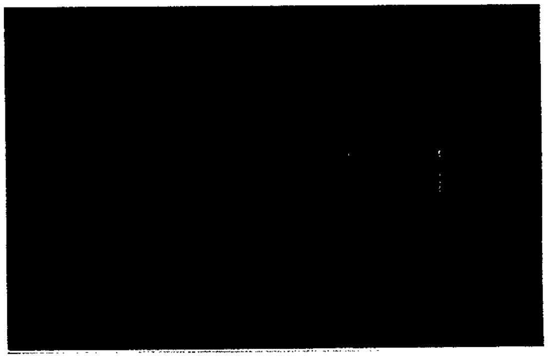


Figure 2. Photograph of DAP-doped silica aerogel monoliths under UV (365 nm) light; Left: bulk-modified; Middle: base-catalyzed post-doped; Right: acid-catalyzed post-doped. Post-doping leads to confinement of DAP only within a thin skin close to the geometrical boundary of the monolith.

Interestingly, my lab was supported by AFOSR at the time that this research was conducted, while Debra's lab was supported by ONR and DARPA; therefore, our paper (*Chem. Mater.* **1999,** *11*, 2837-2845) acknowledges three different branches of the Department of Defense!

(c) Optical Switches Through Photoinduced Electron Transfer in Doped Sol-Gel Materials. In this project (initiated with AFOSR funding but currently funded through a PRF AC-type grant) we utilize and combine our expertise on: (1) sol-gel chemistry; (2) microfabrication technology; and, (3) the photo-chemistry/photophysics of ruthenium complexes.

As was mentioned above, with funding from the AFOSR we have established our own 0.5 μm-resolution fabrication lab within the Chemistry Department of UMR. We are currently using this facility to develop methods for patterning silica sol-gel films (Figure 3).

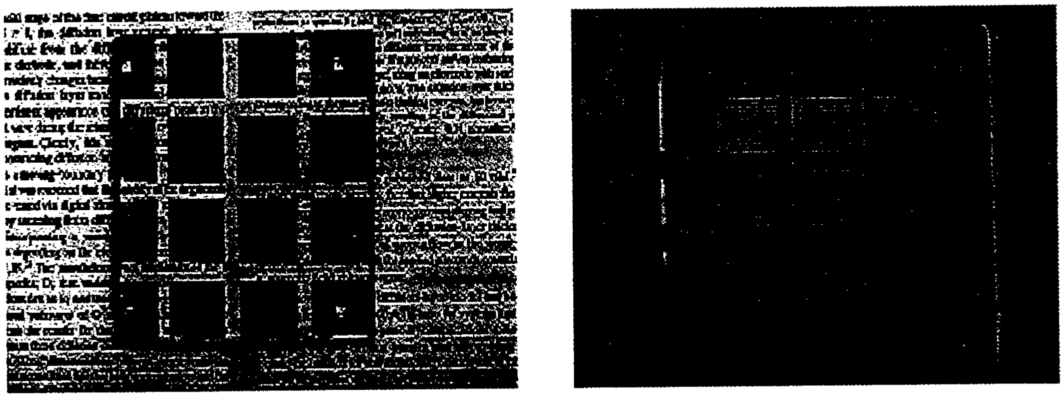
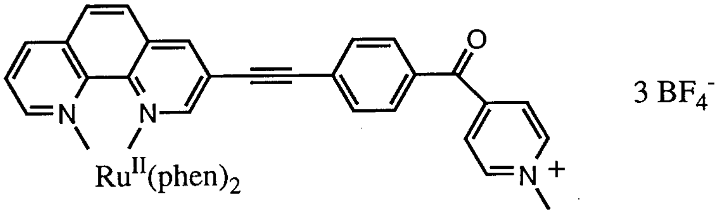


Figure 3. Photolithographically patterned silica sol-gel films (~6 mm thick) on 3'x3' glass substrates and doped with methylene blue. Left: bulk modified film. Right: post-doped film.

Simultaneously we are working on the synthesis of ruthenium complex-electron acceptor dyads such as:



These molecules will be incorporated as dopants in patterned sol-gel films in order to demonstrate nanosecond optical switches operating exclusively in the optical domain. The synthesis of the 4-benzoyl-*N*-methylpyridinium moiety of the above complex was accomplished through funding from our AFOSR grant. Since the redox chemistry of this class of compounds was unknown, we pursued it, and have submitted a manuscript to *J. Phys. Chem. B.*

(d) Magnetohydrodynamic Effects on Electrochemical Systems. Guided by the rigorous hydrodynamic equations, we have identified, isolated and experimentally studied the effect of all parameters controlling electrochemical magnetohydrodynamic convection. Using conventional disk electrodes in magnetic fields (1-2 T) we have demonstrated convective effects equivalent to those obtained during electrode rotation at about 100 rpm, and we have developed equation 2,

$$i_l = 4.3\ 10^2\ n^{3/2} F\ A^{3/4} B^{1/3} C_{bulk}{}^{4/3} D\ \nu^{-1/4} \qquad \text{eq.[2]}$$

which is the magnetic field counterpart of the Levich equation for the rotating electrode (i_l: mass-transfer limited current; n; number of electrons involved in the redox process; F: Faraday constant; A: electrode area; $|\mathbf{B}|$: magnetic field intensity; C_{bulk}: bulk concentration of the redox-active species; D: diffusion coefficient of the redox-active species; and , ν: kinematic viscosity of the electrolytic solution). Magnetohydrodynamic voltammograms have been simulated using a moving boundary diffusion layer model (*J. Phys. Chem. B* **1999**, *103*, 5832-5840; *J. Phys. Chem. B* **1998**, *102*, 3512-3522).

While explaining the data proving that $i_l \sim n^{3/2}$, we stumbled across an interesting observation: a diffusion controlled electrochemical method such as sampled current voltammetry, and a convection dominated one such as rotating disk electrode voltammetry, both yield equal current ratios from two- versus one-electron processes. We pursued that observation further, and currently have a manuscript in press for the special issue of *J. Electroanal. Chem.* honoring Roger Parsons. In that paper we demonstrate further how the two-electron versus one-electron current ratio can be used in combination with computer simulations for determining electron transfer rate constants and diffusion coefficients.

In light of the long-standing debate on the effect of the magnetic field on living systems, we are currently investigating the effect of the magnetic field on the rate of heterogeneous electron transfer. Since magnetohydrodynamic convection is the only means of generating stirring without moving parts, we are currently working also on the design of bench-top magnetoelectrochemical systems for pumping, microfluidics, and microchromatographic separations employing small powerful Nd-Fe-B magnets. In the near future, we will work on the simulation of magnetohydrodynamic convection from first principles of mass, momentum and charge transfer. I have been invited to give an one-hour lecture on our activities in this area in the next Electrochemical Gordon Conference.

Current List of Publications Resulted from AFOSR F49620-94-1-0449

14. "Magnetohydrodynamic Voltammetry with Nd-Fe-B Permanent Magnets. Theory and Experiment," N. Leventis, X. Gao (in preparation for *J. Phys. Chem B*).
13. "Millimeter-Scale Organization in Silica Aerogel Monoliths by Magnetic Alignment of Micron-Size Iron Particles," N. Leventis, I. A. Elder and D. R. Rolison (in preparation for *Advanced Materials*).
12. "Photolithographic Patterning and Doping of Silica Sol-gel Films," N. Leventis, X. Gao, C. Sotiriou-Leventis, and K. R. Gaston (in preparation for *Chemistry of Materials*).
11. "The Redox Chemistry of (4-Benzoyl)-*N*-methylpyridinium Cations in Acetonitrile With and Without Proton Donors; The Role of Hydrogen Bonding during Electrochemical and Photoinduced Electron Transfer Reduction," N. Leventis, I. A. Elder, X. Gao, E. W. Bohannan, C. Sotiriou-Leventis, A.-M. M. Rawashdeh, and K. R. Gaston. Submitted to *J. Phys. Chem. B* (October 2000).
10. "In the Presence of Very Fast Comproportionation, Sampled Current Voltammetry and Rotating Disk Electrode Voltammetry Yield Equal Two- versus One-Electron Limiting Current Ratios. Reconciliation Through Analysis of Concentration Profiles," N. Leventis, and X. Gao *J. Electroanal. Chem.* (In the press for the special issue honoring the 40 years of service of Prof. Roger Parsons as the Journal Editor.)
9. "Durable Modification of Silica Aerogel Monoliths with Fluorescent 2,7-Diazapyrenium Moieties - Sensing Oxygen near the Speed of Open-Air Diffusion," N. Leventis, I. A. Elder, D. R. Rolison, M. L. Anderson, and C. I. Merzbacher *Chem. Mater.* **1999**, *11*, 2837-2845.
8. "Steady-State Voltammetry with Stationary Disk Millielectrodes in Magnetic Fields: Non-Linear Dependence of the Mass-Transfer Limited Current on the Electron Balance of the Faradaic Process," N. Leventis and X. Gao *J. Phys. Chem. B* **1999**, *103*, 5832-5840.

7. “Electrochemistry with Disk and Ring-Disk Millielectrodes in Magnetic Fields,” N. Leventis, M. Chen X. Gao, M. Canalas, and P. Zhang *J. Phys. Chem. B* **1998**, *102*, 3512-3522.
6. “Crosstalk-Free Solution-Phase Electrochromic Matrix Arrays,” N. Leventis, M. Chen, A. I. Liapis, J. W. Johnson, and A. Jain *J. Electrochem. Soc.* **1998**, *145(4),* L55-L58.
5. “Electrochemical Evidence for the Affinity of *n*-Alkyl Sulfonate Group-Modified Viologens to Gold,” N. Leventis, C. Sotiriou-Leventis, M. Chen, and A. Jain *J. Electrochem. Soc.* **1997**, *144(11),* L305-L308.
4. “Electrochemically Assisted Sol-Gel Process for the Synthesis of Polysiloxane Films Incorporating Phenothiazine Dyes Analogous to Methylene Blue; Structure and Ion-Transport Properties of the Films via Spectroscopic and Electrochemical Characterization,” N. Leventis, and M. Chen *Chem. Mater.* **1997**, *9(11),* 2621-2631. (Special issue dedicated to sol-gel derived materials.)
3. “Synthesis of Substituted Phenothiazines Analogous to Methylene Blue by Electrophilic and Nucleophilic Aromatic Substitutions in Tandem. A Mechanistic Perspective,” N. Leventis, M. Chen, and C. Sotiriou-Leventis *Tetrahedron* **1997**, *53(29),* 10083-10092. (Issue honoring W. von Eggers Doering.)
2. "Synthesis of Methylene Blue Modified with Trimethoxysilyl Groups, and Electrode Surface Derivatization," N. Leventis, M. Chen *Polym. Mater. Sci. Eng. Prepr.* **1995**, *73*, 406-407.
1. "Electroluminescent Polymers," N. Leventis, L. Y. Huang *POLYMER NEWS* **1995**, *20*, 307-313 (invited review article).