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19. ABSTRACT (Continue on reverse if necessary and identify by block number) Reversible electroactive doping of conducting polymers was studied with a view toward the determination of important electroactive mechanisms in the polymers. Also the transport of solutes in polymer films was investigated. Research eventually focused on polyaniline where various modified Donnan phenomena were investigated both by means of theory and experiment. Films formed from proton doped emeraldine base proved to be a remarkably efficient gas selective membrane. The mechanism of this process was studied, also by means of theory and experiment. Proton doped polyaniline may be the most universal membrane for gas separations, and possibly the most important technological fallout of basic research on conducting polymers. Besides a number of publications in scientific journals, a patent has been granted to the use of doped conducting polymer films for separation.					
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Principal Investigator: Howard Reiss
Department of Chemistry & Biochemistry
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Personnel: Professor Howard Reiss, UCLA
Professor Pierre Chartier, Université Louis Pasteur, Strasbourg,
France
Professor R. B. Kaner, UCLA
Mr. Mark Anderson (now Dr. Anderson), Ph.D. Thesis, UCLA
Dr. H. M. Ellerby, UCLA
Mr. B. R. Mattes (now Dr. Mattes), Ph.D. Thesis, UCLA
Ms. Jean Conklin, Ph.D. Thesis, UCLA

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PUBLICATIONS

M. R. Anderson, B. R. Mattes, H. Reiss, and R. B. Kaner, Science **252**, 1412 (1991)

M. R. Anderson, B. R. Mattes, R. B. Kaner, Synthetic Metals **41-43**, 1151 (1991)

B. R. Mattes, M. R. Anderson, H. Reiss, and R. B. Kaner in "Intrinsically Conducting Polymers", M. Aldissi, ed. (Kluwer Academic Publishing, Dordrecht, The Netherlands, in press).

B. R. Mattes, M. R. Anderson, J. A. Conklin, H. Reiss, and R. B. Kaner, Synthetic Metals **55-57**, 3655 (1993).

H. Reiss, M. R. Anderson and W. D. Murphy, "Effect of Inhomogeneous Stress on the Selectivity of Membranes", submitted to the Journal of Membrane Science.

H. Reiss, "Possible Mechanisms for the Gas Selective Properties of Emeraldine Membranes" in Proceedings of Nobel Symposium 81 (Conjugated Polymers) p. 263 (Oxford University Press, 1993).

P. Chartier, B. Mattes, and H. Reiss, J. Phys. Chem. **96**, 3556 (1992).

P. Chartier, B. Mattes, and H. Reiss, J. Phys. Chem. **96**, 5501 (1992).

Paper by J. Masters, A. G. MacDiarmid, and H. Reiss on "Internal Redox Phenomena of Polyaniline in NMP", in preparation.

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93-24328



PATENT

U.S. Patent No. 5096586

"Membranes Having Selective Permeability"

March 17, 1992

Awarded to: R. B. Kaner, M. T. Anderson, B. R. Mattes, and H. Reiss

Assigned to: The Regents of the University of California

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS

The research under this grant was directed toward the study of various physical chemical phenomena associated with the electroactive doping of conducting polymers and to the response, in terms of both equilibrium and transport phenomena, of such doped polymers to various chemical agents. In meeting these goals the research program was aimed at demonstrating the occurrence of thermodynamically reversible equilibrium in the doping of such polymers and the use of such equilibria in the study of internal polymer features such as band structures and the natures of current carriers. Impact on the doping process itself was of interest. In addition, the research was aimed at the study of conducting polymer films as membranes for gas separation (transport) and the possible development of an outstanding membrane for this purpose.

As it turned out most of the research became focused on polyaniline because of the discovery of its remarkable ability to separate gases. The equilibrium features that became the center of interest then involved the proton doping of polyaniline and the so-called "modified Donnan equilibria" associated with the fact that adsorbed protons though strongly bound, were not irrevocably fixed. The study of transport properties became focused on the transport of penetrants through polyaniline films. Both experimental and theoretical studies were performed.

Normally, Donnan equilibria are investigated in connection with ion exchange membranes and it is the partitioning of free cations and anions between a bathing electrolyte solution and the membrane that is of primary interest. In the case of polyaniline, the partitioning of the tightly bound protons must also be considered and the Donnan phenomenon plays an important role in the electroactive doping of the polymer and in the stability of the doped state as a function of the pH of the membrane environment. Furthermore the potential across the double layer at the membrane-electrolyte interface, the Donnan potential, plays a role in electrochemical applications of the conducting polymer.

A new theory for the Donnan phenomenon had to be developed (because of the "modification") and it was confirmed by experiment. In particular, the theory predicted that the adsorbed protons could be retained, even at very high levels of pH, if polyaniline was blended with polyvinylsulfonate, and therefore "self-doped". Again theory and experiment were in agreement. Thus the theory produced a practical result.

Other studies of doping equilibria involved halogen acids in the gaseous state and were useful for the preparation of gas selective membranes.

As a by-product of the studies of the modified Donnan phenomenon, a technique was discovered for directly measuring the charge in the Donnan space charge layer. No direct means of accomplishing this had been previously available for a double layer involving a solid phase. The information was also useful in the characterization of the Donnan phenomenon and the electroactive properties of the polymer.

A very large portion of the research under the Grant involved the study of the remarkable gas selective membrane that could be prepared by doping films prepared from emeraldine base with protons. In this effort, the principal investigator collaborated with Professor Kaner and his group who were largely responsible for innovative membrane preparation. In addition Professor Kaner's group now operates the laboratory that was developed, under the grant, for the study of membrane permeability so that important measurements will continue with the support of other funds.

The salient feature in the establishment of high separation factors for gases seems to be a reversible proton doping cycle that allows one to maximize the separation factor. Considerable study of the process was involved (and other conducting polymer -- dopant systems, besides polyaniline, were also studied). The mechanism is not fully understood although it seems to be based on the ability to "fine tune" percolative channel networks by controlling morphological and conformational changes that occur on the mesoscopic scale when polyaniline is doped with protons. Under the grant, a new theory of membrane selectivity has been developed, based on the idea that stress fields that have spatial variations on the mesoscopic scale can improve selectivity. Such fluctuating stresses could easily result from the morphological changes mentioned above. The theory is applicable to polymers in general.

The most remarkable separation, accomplished with these membranes seems to be that of oxygen and nitrogen, where the separation factor, O_2/N_2 , has been confirmed, by grant work, at levels as high as 28, and, by other laboratories, at a level of 16. Normally (with other membranes) this separation factor is less than 10. Among other things the high separation factor seems to be due to a (measured) increase of O_2 solubility associated with proton doping.

When the necessary development work involving this membrane is complete, it could very well be one of the most practical consequences of the discovery of conducting polymers. As indicated above, a U.S. patent has been granted that covers polyaniline and other conducting polymers as membranes for separation.

AFOSR Program Manager: Dr. Charles Lee.

Final Technical Report

Grant No. AFOSR-89-0425

**Principal Investigator : Professor Howard Reiss
Department of Chemistry & Biochemistry
University of California, Los Angeles**

Introduction

Research under AFOSR grant # 89-0425A focused mainly on polyaniline, its derivatives, and its blends in both doped and undoped states. An important part of the overall research program was concerned with the use of doped polyaniline as an unusually promising membrane for gas separations. Other conducting polymers such as polydimethoxyparaphenylenevinylene (DMPPV) doped with FeCl_3 were examined for this purpose.

Another part of the research, funded by the grant, involved the study of "modified Donnan phenomena in polyaniline. This research was important for the characterization of proton adsorption isotherms in polyaniline and for the design of methods for the maintenance of doping stability over wide ranges of bathing solution pH. As a by-product of these studies a method was devised for the direct measurement of the charge in an electrical double layer. Derivative studies involving further work on the modified Donnan equilibrium were undertaken as direct consequences of the Donnan work supported by the grant but were supported by other funds. Also, as a consequence of work initiated under the grant, a very detailed theoretical study dealing with transport in ion exchange membranes was undertaken. This work, also supported by other funds, constituted a very substantial advance in our understanding of the nonequilibrium behavior of ion exchange membranes.

Finally, our work on membrane separations has resulted in the award of a patent, namely:

"Membranes Having Selective Permeability"

U. S. Patent No. 5096586

March 17, 1992

Granted to: R. B. Kaner, M. R. Anderson,
B. R. Mattes, and H. Reiss

Assigned to: The Regents of the University of California

Brief commentary, augmented by appropriate referencing, on these various accomplishments is presented below.

I. Polyaniline as a Membrane for Gas Separations

1. The emeraldine form of polyaniline has been shown to be an excellent separator of various gas pairs. The separation factor can be optimized by subjecting

emeraldine films to a reversible proton doping process using aqueous HCl or other halogen acids. Pairs that are subject to good separation are H₂/N₂, He/N₂, O₂/N₂ and CO₂/CH₄. the important O₂/N₂ separation appears to be due to an increase in O₂ solubility due to paramagnetic interactions. Papers reporting these various studies are:

M. R. Anderson, B. R. Mattes, H. Reiss, and R. B. Kaner, *Science*, **252**, 1412 (1991).

M. R. Anderson, B. R. Mattes, H. Reiss, and R. B. Kaner, *Synthetic Metals* **41-43**, 1151 (1991).

B. R. Mattes, M. R. Anderson, H. Reiss, and R. B. Kaner in "Intrinsically Conducting Polymers", M. Aldissi, ed. (Kluwer Academic Publishing, Dordrecht, Netherlands, in press).

2. Studies on the preparation of polyaniline films and the specific effects of doping, curing time, as well on the gas separation behaviors of polydimethoxyparaphenylenevinylene (DMPPV) and blended polyaniline-polyimide films were performed. The additional findings show how selective control of gas permeability is facilitated by the doping, undoping and redoping (cycling) process of emeraldine films. Specifically, permeability data for H₂, He, CH₄, CO₂, O₂, N₂ and CH₄ were determined for films treated with perchloric acid. There is a large increase in permeability to all gases following the doping and undoping film treatment cycle. Moreover, controlled redoping (of the undoped films) results in large separation factors for industrially important gas pairs. These results are consistent with the model based on dopant occupation of free-volume of the "pin-hole free" film. This cycling phenomenon was also found in other conjugated polymers such as polydimethoxyparaphenylenevinylene (DMPPV). Another important variable for gas transport properties of polyaniline films is the film curing time. Permeability data for films cured at 125° C for 2, 3, and 6 hours, and then cycled, indicate that a three hour cure time produces the most fully dense films. Preliminary gas permeability data for a polyimide thin film by itself and, a polyimide blend containing polyaniline were obtained.

The relevant publication is:

B. R. Mattes, M. R. Anderson, J. A. Conklin, H. Reiss, and R. B. Kaner, *Synthetic Metals*, **55-57**, 3655 (1993).

3. Emeraldine base was proton doped from the gas phase using HF, HCl, HBr, and HI, and then dedoped using NH₃. Preliminary results show an approximate inversion of the order of the resulting permeabilities for various penetrant gases from that found when the same dopants are introduced via aqueous solution. The difference is ascribed to the solvation shell of the anion when aqueous solution is used. However residual salt, after dedoping, somewhat clouds the issue. A publication is not yet available, but preliminary details can be found in:

M. R. Anderson, Ph.D. Thesis "An Investigation of Conducting Polymer Materials as Gas Separation Membranes", University of California, Los Angeles, 1992.

4. In order to explain the unusual properties of proton doped polyaniline as a membrane for gas separations, a theory was developed in which fluctuations of stress on a mesoscopic length scale could improve the separation factor. The theory was motivated by the fact that, upon proton doping, polyaniline is observed to undergo dramatic morphological and conformational changes that can produce such fluctuating stress fields. The theory is thought to have general application, beyond conducting polymer membranes.

In the actual theory, stress undergoing spatial fluctuations on a mesoscopic length scale is shown to be capable of increasing the separation factors of membrane-penetrant systems, provided it is of sufficient magnitude, i.e., if the ratio of the stored elastic energy to the thermal energy exceeds unity. The theory is developed in schematic form for a one dimensional case and is used to demonstrate that membranes consisting of glassy polymers can meet the stated criterion. Extrapolation to the three dimensional case indicates that such fluctuating stresses produce "blurred supersieves" in which the widths of the channels depend on the partial molar volumes of the penetrants in the membrane phase. This effect accounts for the increased selectivity. The theory also predicts the frequently observed behavior in which increased selectivity is accompanied by decreased membrane permeability. The theory is not in conflict with most of the conventional theories of membrane selectivity where mechanisms are considered on the molecular scale of length so that these mechanisms could still be operative while the new mechanism simply enhances the separation factor based on the conventional ones.

It is suggested that treatments of membranes that lead to morphological heterogeneity on the mesoscopic scale can produce the desired fluctuating stress fields.

Progress has been made on a true three dimensional theory.

A paper describing the theory has been submitted to the Journal of Membrane Science and may be referenced as :

H. Reiss, M. R. Anderson and W. D. Murphy, "Effect of Inhomogeneous Stress on the Selectivity of Membranes", submitted to the Journal of Membrane Science.

A preprint of this paper accompanies this report. Also an earlier (preliminary) paper has been published in the Proceedings of Nobel Symposium 81. The precise reference is:

H. Reiss, "Possible Mechanism for the Gas Selective Properties of Emeraldine Membranes" in Proceedings of Nobel Symposium 81 (Conjugated Polymers) p. 263 (Oxford University Press, 1993).

II. Modified Donnan Phenomena and Other Equilibria Involving Polyaniline

1. We recognized that a proton doped polyaniline film constituted an ion exchange membrane in which the "fixed" ions were the adsorbed protons. Fixed ions give rise to a so-called Donnan equilibrium between a membrane and a bathing electrolyte solution. This equilibrium causes the membrane to be selective for ions charged oppositely to fixed ions. Furthermore, a charged double layer forms at the interface between the membrane and the bathing electrolyte solution giving rise to a electrical potential known as the Donnan potential.

When the "fixed" ions are not irrevocably fixed like the protons adsorbed by polyaniline, their concentration in membranes, just as the concentrations of other ions, is dependent on the Donnan equilibrium. Then we deal with a "modified" Donnan equilibrium which controls the doping process itself. The theory of this modified Donnan phenomenon had not been previously formulated. As a result we worked out the theory and performed experiments to check it for the case of polyaniline.

Further work was stimulated by this initial effort. The additional work was not supported by the AFOSR grant (because of lack of funds) but it was certainly

stimulated by the AFOSR study. Among the accomplishments of this further work was the important discovery of means to stabilize the proton dopant even in solutions of high pH. The relevant papers are:

P. Chartier, B. Mattes, and H. Reiss, *J. Phys. Chem.* **96**, 3556 (1992), (supported by grant #AFOSR-89-0425).

S. Mafé, J. A. Manzanares, and H. Reiss, *J. Chem. Phys.* **98**, 2408 (1993), (not supported by the grant).

S. Mafé, J. A. Manzanares, and H. Reiss, *J. Chem. Phys.* **98**, 2408 (1993), (not supported by the grant).

2. As a by-product of our studies on the modified Donnan Phenomenon, a means was discovered for measuring the charge in a double layer directly. The relevant paper is:

P. Charier, B. Mattes, and H. Reiss, *J. Phys. Chem.* **96**, 5501 (1992).

3. In collaboration with A. G. MacDiarmid and J. Masters of the University of Pennsylvania we studied some extremely interesting phenomena dealing with internal redox equilibria of polyaniline in NMP solution.

It was discovered the leucoemeraldine base and pernigraniline base, both dissolved in NMP, established a reversible chemical equilibrium involving, as a product, emeraldine base. This process is one of internal redox in which pernigraniline oxidizes leucoemeraldine. The absorption spectra of these solutions contain isobestic points and other regularities that, when combined with appropriate statistical mechanical theory, demonstrate that the reaction achieves equilibrium and that this equilibrium is strongly shifted toward the product. Furthermore, it was also demonstrated that no polyaniline oxidation state other than those associated leucoemeraldine, emeraldine, and pernigraniline exists in NMP solution.

A paper describing this work is in preparation.