4

OFFICE OF NAVAL RESEARCH

END-OF-THE-YEAR REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/
HONORS/STUDENT REPORT

for

CONTRACT N00014-90-J-1156

R&T Code 413d003

Novel Electrochemical Materials Prepared by Sol-Gel Chemistry

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and subcontracts to

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31 May 1993

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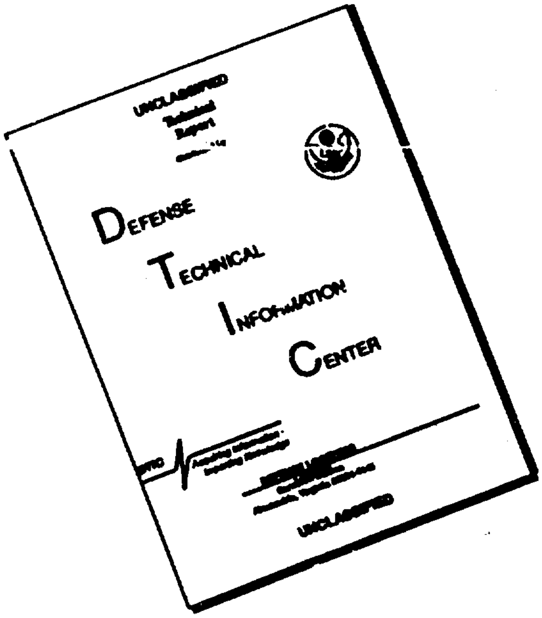

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OFFICE OF NAVAL RESEARCH
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT

R&T Number: 413d003
Contract/Grant Number: N00014-90-J-1156
Contract /Grant Title: Novel Electrochemical Materials Prepared by Sol-Gel
Chemistry
Principal Investigator Gregory C. Farrington
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Pennsylvania 220 S. 33rd Street, Philadelphia, PA 19104-6391

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a. Number of papers submitted to refereed journals, but not published: 2
b. * Number of papers published in refereed journals (for each, provide a complete citation): 7
c. Number of books or chapters submitted, but not yet published: 0
d. * Number of books or chapters published (for each, provide a complete citation): 1
e. * Number of printed technical reports/non-refereed papers (for each, provide a complete citation): 0
f. Number of Patents filed: 0
g. * Number of patents granted (for each, provide a complete citation): 0
h. * Number of invited presentations (for each, provide a complete citation): 5
i. * Number of submitted presentations (for each, provide a complete citation): 3
j. * Honors/Awards/Prizes for contract/grant employees (list attached): 1
k. Total number of Full-time equivalent Graduate Students and Post Doctoral associates supported during this period, under <u>this</u> R&T project number:
    Graduate Students: 4
    Post-Doctoral Associates: 1
  including the number of,
    Female Graduate Students: 1
    Female Post Doctoral Associates: 0
  the number of
    Minority* Graduate Students: 0
    Minority* Post Doctoral Associates: 0
  and, the number of
    Asian Graduate Students: 1
    Asian Post Doctoral Associates: 0
l. * Other funding (list agency, grant title, amount received this year, total amount, period of performance and a brief statement regarding the relationship of that research to your ONR grant)

* Use the letter and an appropriate title as a heading for your list, e.g.:
b. Published Papers in Refereed Journals, or, d. Books and Chapters published
Also submit the citation lists as ASCII files, preferably on a 3" or 5" PC-compatible floppy disk

*Minorities include Blacks, Aleuts, Amindians, Hispanics, etc. NB: Asians are not considered an under-represented or minority group in science and engineering.

Part I.

a. Papers Submitted to Refereed Journals:

Bruce Katz, Ian Mann, Like Xie, Rokeya Huq, Gregory C. Farrington, "Electrical and Electrochemical Characteristics of V_2O_5 Xerogel Nanocomposites," presented at The Electrochemical Society, Honolulu, Hawaii, May 1993

Krzysztof Kowal, Like Xie, Rokeya Huq, and Gregory C. Farrington"In-Situ Atomic Force Microscopy Study of the Plating and Stripping of Silver," presented at ECS Meeting in Hawaii, May 1993

b. Papers Published in Refereed Journals:

T. Gustafsson, J.O. Thomas, R. Koksbang, and G.C. Farrington, "The Polymer Battery as an Environment for *in situ* X-ray Diffraction Studies of Solid-State Electrochemical Processes," Electrochimica Acta, Vol. 37, No.9, pp. 1639-1644, July 1992.

R. Huq, R. Koksbang, P.E. Tonder, and G.C. Farrington, "Effect of Plasticizers on the Properties of New Ambient Temperature Polymer Electrolyte," Electrochimica Acta, Vol. 37, No. 9, pp. 1681-1684, July 1992.

J.O. Thomas, "What Can Diffraction Tell Us About Mobile Ions? Solid State Ionics," 53-56 1311 (1992)

S. Edvardsson, M. Wolf & J.O. Thomas, "The Sensitivity of Optical Absorption Intensities for Rare-Earth Ions," Phys.Rev. B45 10918 (1992)

M.A.Zendejas & J.O. Thomas, "Conduction Mechanisms in Solid Electrolytes: Mg^{2+} Stabilized β-Alumina," Phys. Scripta. 47 440 (1993)

M. Wolf, A. Wendsjo, J.O. Thomas & J.D. Barrie, "The Structure of the Luminescent System Na^+/UO_2^{2+} β″-Alumina," Acta Cryst. B. (In press)

M. Wolf & J.O. Thomas, "The Ionic Distribution in the Solid State Laser Material Na^+/Nd^{3+} β″-Alumina," Acta Cryst. B. (In press)

c. Books or Chapters Submitted for Publication:

d. Books (and sections) Published:

J.O. Thomas & M.A. Zendejas, "Molecular Dynamics Simulation in the Design of Solid Ionics." Chapter in: "Solid State Ionics: Materials and Applications." Ed. B.V.R. Chowdari *et al.*, pp. 19-28. World Sci. Publ., Singapore. 1992

e. **Printed Technical Reports and Non-referred Papers**

f. **Patents Filed**

g. **Patents Granted**

h. **Invited Presentations at Workshops or Professional Society Meetings**

M. Wolf, S. Edvardsson & J.O. Thomas, "Molecular Dynamics Simulation Based Analysis of Optical Absorption Spectra for Na^+/Nd^{3+} β"-Alumina,"*At* : Physics and Chemistry of Luminescent Materials Symposium at the Fall ECS Meeting, Toronto, October 1992

J.O. Thomas & M.A. Zendejas, "Molecular Dynamics Simulation in the Design of Solid Ionics" at Third Asian Solid State Ionics Conference, Varanasi, India, November 1992

G. C. Farrington and L. Xie, " Molecular Dynamics Simulation of Ion Motion in Polymer and Gel Electrolytes," Workshop on Solid Polymer Electrolytes, Gothenberg, Sweden, August 1992

G. C. Farrington and L. Xie, " Molecular Dynamics Simulation of Ion Motion in Polymer and Gel Electrolytes," Symposium on Polymer Electrolytes, Materials Research Society, December 1992

M. S. Mendolia, R. Huq, and G. C. Farrington, "Synthesis and Characterization of Novel Lithium Gel Electrolytes," presented at The Electrochemical Society, Honolulu, Hawaii, May 1993

Bruce Katz, Ian Mann, Like Xie, Rokeya Huq, Gregory C. Farrington, "Electrical and Electrochemical Characteristics of V_2O_5 Xerogel Nanocomposites," presented at The Electrochemical Society, Honolulu, Hawaii, May 1993

i. Contributed Presentations at Workshops and Professional Society Meetings

M. Wolf, S. Edvardsson & J.O. Thomas, "A Molecular Dynamics Based Treatment of Judd-Ofelt Theory for Rare-Earth Ions in Solids"
At: US - France Workshop on the Chemistry of Optical Materials.
Maubisson, France. Sept. 1992

Krzysztof Kowal, Like Xie, Rokeya Huq, and Gregory C.Farrington, "In-Situ Atomic Force Microscopy Study of the Plating and Stripping of Silver," presented at ECS Meeting in Hawaii, May 1993

Bruce Katz, Ian Mann, Like Xie, Rokeya Huq, Gregory C. Farrington, "Electrical and Electrochemical Characteristics of V_2O_5 Xerogel Nanocomposites," presented at ECS Meeting in Hawaii, May 1993

j. Honors/Awards/Prizes

Project responsible J.O. Thomas promoted to Chair of Structural Chemistry at Uppsala University, December 1992

l. Other funding

1. NSF (DMR 88 19885): Ionically Conductive Solids
   Amount Received this year: $42,000
   Total Amount: $42,000
   Period 9/1/92 - 6/30/93

2. ONR (N00014 91-J-4028): Electrochemistry and Energy Storage Polymer Solvents
   Amount Received this year: $657,430
   Total Amount: $2,078,752
   Period 7/91 - 2/94

3. Hughes Aircraft Corp.: Support of Polymers Research
   Amount Received this year: $13,000
   Total Amount: $13,000
   Period: 9/1/91 - 12/31/92

END OF THE YEAR REPORT - Part II
31 May 1992

a. Principal Investigator: Gregory C. Farrington
Department of Materials Science and Engineering
University of Pennsylvania
220 South 33rd. Street
Philadelphia, PA 19104

b. Telephone Number: 215-898-6642

c. ONR Scientific Officer: Dr. Robert J. Nowak

d. Project Description:

Past efforts in this program have been devoted to exploring the preparation, properties, and structures of various beta" alumina compositions in which the mobile sodium ion content was replaced with a variety of divalent and trivalent cations. Though this line of work has produced a great number of new and unusual materials, in particular unusual solid electrolytes and new optical materials, as well as insight into the factors which control fast ion transport in solids, it seemed an appropriate time to move on to another topic. So, over the past year, most of the effort in this program has been devoted to investigations of the use of sol-gel chemistry to produce unusual electrochemical materials, such as solid state ionic conductors, new high rate cathode materials, and unusual organic-inorganic composite materials. This work has proven quite fruitful.

e. Significant Results During Last Year:

Studies of Transition Metal Oxide Xerogels
University of Pennsylvania

Some of the most interesting sol-gel derived transition metal oxides can be formed into thin films with virtually no thermal treatment, which allows the films to retain the structure present in the gel phase. These films, known as xerogels, are often diphasic with curious properties that are closely related to their unique structure.

Vanadium pentoxide xerogels exhibit a wide variety of properties and are the most studied xerogel to date. Work at Penn is focussed on understanding the properties of these materials and how they are related both structure and microstructure.

The study of the vanadium pentoxide xerogels also lays the groundwork for future studies of other transition metal xerogels such as tungsten oxide and molybdenum oxide. Work on these systems is also being pursued.

Conductivity Studies

Vanadium pentoxide xerogels are essentially oxide hydrates exhibiting both electronic conduction in the oxide phase and ionic conduction in the solvent phase. Electrical conductivity values reported in the literature vary from 10^{-6} S/cm to 1 S/cm. We are working to understand the factors that lead to such a wide variation in conductivity.

Initial studies of the conductivity of vanadium oxide xerogels indicates there are at least two conductivity domains, the first dominated by ionic conduction in the solvent phase and the second by electronic conduction in the oxide. As the temperature of the xerogel is raised in air, water is removed from the system, and the total conductivity decreases as the proton mobility is lowered. With a further increase in temperature the conductivity begins to rise, behavior typical of small polaron hopping. Upon cooling to room temperature in an inert atmosphere, water is not present and therefore cannot re-enter the xerogel, and the conductivity continues to decrease.

The room temperature conductivity of the hydrated vanadium pentoxide xerogel is dominated by protonic conductivity is on the order of 0.05 S/cm. When water is removed the conduction is essentially electronic in nature and is typically 0.001 S/cm. The specific magnitude of the electronic conductivity depends on several factors, most importantly the amount of reduced vanadium in the coating. Vanadium pentoxide xerogels may undergo spontaneous reduction in air and, with time, the ratio of V^{4+}/V^{5+} increases.

Electrochemical Lithiation

Electrochemical intercalation of lithium is known to occur in a variety of crystalline and amorphous inorganic compounds. While there are relatively few reports on lithium intercalation into amorphous V_2O_5, crystalline V_2O_5 bronzes have been extensively investigated.

Vanadium pentoxide xerogels are derived directly from the gel phase and have a unique structure somewhere between amorphous and crystalline. The nature of the structure is reflected in the electrochemical characteristics of the lithium intercalation in the xerogel. Cyclic voltamagrams may exhibit both amorphous and crystalline behavior depending on sample preparation and pre-treatment prior to electrochemical reaction. Not surprisingly some research groups have reported crystalline behavior while others suggest a more amorphous type of intercalation response. The differences may be related to the ageing process of the xerogel and its ability to co-interalate the electrolyte during electrochemical cycling.

Nano-Composites of V_2O_5 and Polyaniline

Vanadium pentoxide xerogels have the ability to undergo intercalation polymerization reactions, whereby monomers are intercalated into the oxide and are then oxidatively polymerized to form oxide polymer nanocomposites. A particularly interesting nanocomposite is formed with V_2O_5 xerogels and electronically conducting polymers such as polyaniline. Preparation of these systems is relatively simple and can lead to the formation of an intimate electronically conducting polymer and semi-conducting oxide material with a variety of interesting characteristics. Composite films are extremely flexible and can be made free standing. The electrical conductivity increases by almost three orders of magnitude compared to the dehydrated xerogels. The origin of this increase is presently being investigated.

When studying polyaniline it is crucial to be able to determine both its oxidation state and degree of doping. We are presently using UV visible spectroscopy to determine the oxidation state of polyaniline within the V_2O_5-polyaniline nano-composites. The ability of polyaniline to undergo redox reactions and, in turn, change its oxidation state electrochemically may lead to future applications of the nano-composites as cathode materials for secondary lithium batteries. It is interesting to note that polyaniline is presently studied as a cathode material which undergoes anionic intercalation, lithium has never been shown to electrochemically insert into polyaniline. However in the nanocomposites the polymer can undergo redox reactions while the oxide network accomodates the lithium cation. Preliminary studies suggest that intercalation into the nanocomposites is possible, and we are pursuing this area presently.

Xerogel Structure Studies using Electrochemical Atomic Force Microscopy

The properties exhibited by the V_2O_5 xerogels arise from their unusual structure which is directly derived from the structure in the gel state. Investigations into the structural changes that occur during intercalation reactions such as solvent exchange, electrochemical intercalation and polymerization reactions has been limited by the high vacuum requirements of electron microscopy. Atomic force microscopy is a novel technique ideally suited for in-situ studies of the changes that occur during intercalation. The great utility of AFM for intercalation studies is its ability to image while a specimen is in solution and under potential control, allowing for in-situ studies with resolution equal to that obtained with electron microscopy.

Figure 1 is an AFM image of a 3 micron thick vanadium pentoxide xerogel coating. The interesting surface features arise from the ordered aggregation in the gel. The surface appears to consist of elongated fibrous aggregates interwoven within each other. This elongated structure is not surprising when one considers that the gel consists of ribbon-shaped colloids. These ribbon-shaped colloids were previously imaged with TEM. In an attempt to image the colloids with AFM a diluted gel was coated onto glass, figure 2. The microcrystals were on average 1000Å wide, 50Å high and 3 microns long and thus have an extremely large aspect ratio. In fact the microcrystals seen with AFM are are actually microaggregates of the ribbon shaped colloids imaged with TEM. X-ray diffraction studies have clearly demonstrated the orientation and order of the colloids in both the gel and xerogel, if this order is retained in the microcrystals we can begin to describe its internal structure as seen in figure 3. The ability to image these microcrystals with AFM allows us to follow the structural changes occuring during intercalation on a nanometer scale and in three dimensions.

WO_3 Xerogels

Compared with the vanadium pentoxide materials little to no attention has been paid to coatings formed directly from other transition metal oxides. We have prepared thin film coatings directly from tungsten oxide gels. These xerogels exhibit an extensive variety of properties and have a unique structure derived from the gel phase. Figure 4 and 5 are TEM and AFM images of this system. The colloids appear to be disc shaped micro-single crystals. From AFM it appears that the individual discs stack neatly on top of each other when forming a thin film. Figure 6 illustrates this stacking behavior.

f. Summary of Research Plans for the Coming Year

Work proposed for the coming year will focus on preparing novel electrode and electrolyte materials using sol-gel chemical synthetic techniques. The sol-gel route should make it possible to create both new materials and materials in which new phenomena are observed. As one example of the former, sol-gel synthesis should make it possible to prepare materials which cannot be created by more conventional chemical routes, such as complex mixed transition metal oxides which do not exist as high temperature crystalline phases but may have potential as high energy density cathode materials. Another is in unusual composite materials in which, for example, an ionically or electronically conductive polymer is intimately mixed with an inorganic matrix.

Sol-gel synthesis should also make it possible to exploit new phenomena, such those occurring in electrochemical materials in which the surface, instead of being a small fraction of the bulk, for practical purposes *is* the bulk. Aerosols have exceptionally high surface areas and in the material comprising them the surface is at most 100-1000Å from any point in the bulk. In such materials, an intercalation reaction that would occur far too slowly in a crystal of normal dimensions might occur fast enough that it could be used for rapid charge storage. Alternatively, surface conduction processes that would represent minor (or even major) effects in a dense sample should dominate the characteristics of an aerogel that has, for example, an acidic surface on which water is adsorbed. The result should be rather interesting proton conduction processes.

Proposed work will focus on understanding the structural characteristics of vanadium oxide gels especially during solvent exchange and ion insertion reactions. This work will be carried out using electrochemical atomic force microscopy (ECAFM) techniques. Other work will examine the structural and electrochemical characteristics of gels containing extremely large concentrations of dispersed inorganic salts. Another thrust of investigation will focus on understanding the factors that control the rate of ion diffusion and solvent molecule motion in organic gels containing high concentrations of salts dissolved in a non-aqueous solvent.

g. Graduate Students and Postdoctorals Currently Working on the Project

Bruce Katz	(Ph.D. student)
Krsystof Kowal	(Ph.D. student)
Kelly Brown	(Ph.D. student)
Like Xie	(Postdoctoral fellow)

END OF THE YEAR REPORT - Part II

31 May 1992

a. Principal Investigator: John O. Thomas
Institute of Chemistry
University of Uppsala
Uppsala S 751 21, Sweden

b. Telephone Number: 46-18-115644

c. ONR Scientific Officer: Dr. Robert J. Nowak

d. Project Description:

An essential basis for computer-aided design of solid-state laser materials is the calculation of the optical absorption spectrum for potential structures. This involves the evaluation of the field at each of the rare-earth ions in the structure, for subsequent insertion into Judd-Ofelt formalism. Difficulties arise in treating the special type of non-stoichiometric high vacancy-density situation occurring in the RE β''-aluminas. This problem is addressed specifically in the project, with the long-term goal of extending the treatment to amorphous, typically sol-gel synthesized, materials. In this way, a most valuable tool will have been developed in the study of this important class of materials.

e. Significant Results During Last Year:

Our earlier developed molecular dynamics (MD) based treatment of Judd-Ofelt theory governing the optical absorption of rare-earth ions has been applied to two qualitatively different systems: Na^+/Nd^{3+} and Na^+/Er^{3+} β''-alumina. In both cases, remarkably good agreement has been obtained with experimental spectra. The method has thus been demonstrated as a sensitive probe of local environment, and thus as a valuable tool in the design of structurally ill-defined amorphous materials.

MD studies of the β-alumina systems have also led to the important insight that apparently "unproductive" back-and-fore ion jumps can have a critical gating effect for longer range ion jumps in the near vicinity. IR/Raman vibrational spectra have also been calculated;

incorrectly assigned bands in the experimental spectra have been identified and new assignments made.

f. Summary of Research Plans for the Coming Year

Our MD based treatment of optical absorption will be exploited to probe the local environment of monoatomic RE ions and simple molecular ions (e.g. UO_2^{2+}) in sol-gel synthesized inorganic amorphous optical hosts. A subtle interplay of MD simulations and IR/Raman measurements is also envisaged.

Monte Carlo and MD simulation treatments will also be made of V-O systems at different levels of densification - from single-crystal to aerogel. Bulk and surface properties will be analysed with a view to potential electrode applications.

g. Graduate Students and Postdoctorals Currently Working on the Project

Mats Wolf	(Ph.D. student)

Part III.

Molecular Dynamics Aided Design of Solid State Laser Materials
University of Uppsala

Molecular dynamics (MD) based Judd-Ofelt theory - a valuable tool for computer-aided design of solid-laser materials.

Josh Thomas
University of Uppsala
Sweden

Special difficulties arise in the calculation of the optical properties of <u>non-stoichiometric</u> crystalline solids: it is necessary to evaluate the actual electric field at the rare-earth (RE) ions in the material - not the average field calculated on the basis of average structure.

<u>MD simulation</u> provides a natural solution to the problem: the explicit field at each ion in a large simulation box can be evaluated, and the total effective oscillator strength for each of the optical excitations evaluated by an averaging procedure.

Prior to this work, only poor qualitative agreement could be expected from applying Judd-Ofelt theory to non-stoichiometric high vacancy-density systems of type Na^{+}/Nd^{3+} β″-alumina.

The figure shows the excellent agreement obtained with our new approach (paper submitted to Phys Rev.).

The implication here is that we now have a powerful tool for computer-aided design of even more challenging disordered (amorphous) optical materials, where MD simulation represents a unique way of obtaining appropriate local structures around the RE ions.

Part III

TRANSITION METAL OXIDE XEROGELS: STRUCTURE STUDIES USING ATOMIC FORCE MICROSCOPY

University of Pennsylvania

Description of Viewgraphs

The properties exhibited by the V_2O_5 xerogels arise from their unusual structure which is directly derived from the structure in the gel state. Investigations into the structural changes that occur during intercalation reactions such as solvent exchange, electrochemical intercalation and polymerization reactions has been limited by the high vacuum requirements of electron microscopy. Atomic force microscopy is a novel technique ideally suited for in-situ studies of the changes that occur during intercalation. The great utility of AFM for intercalation studies is its ability to image while a specimen is in solution and under potential control, allowing for in-situ studies with resolution equal to that obtained with electron microscopy.

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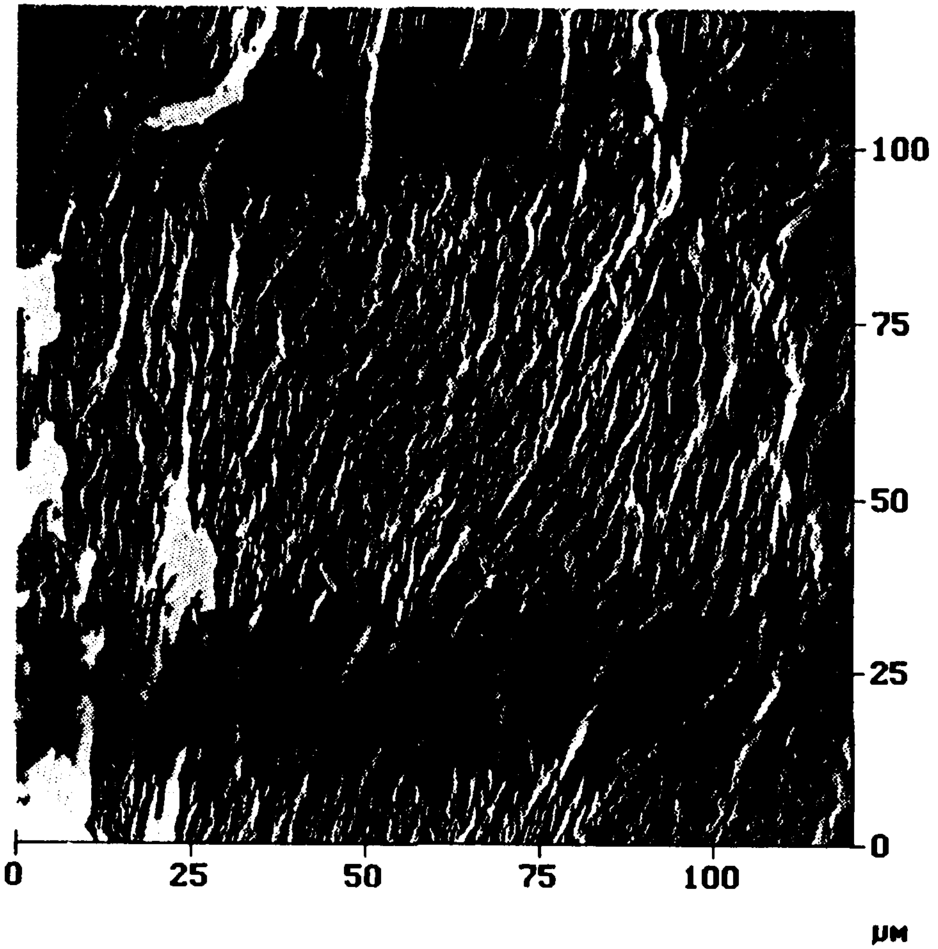
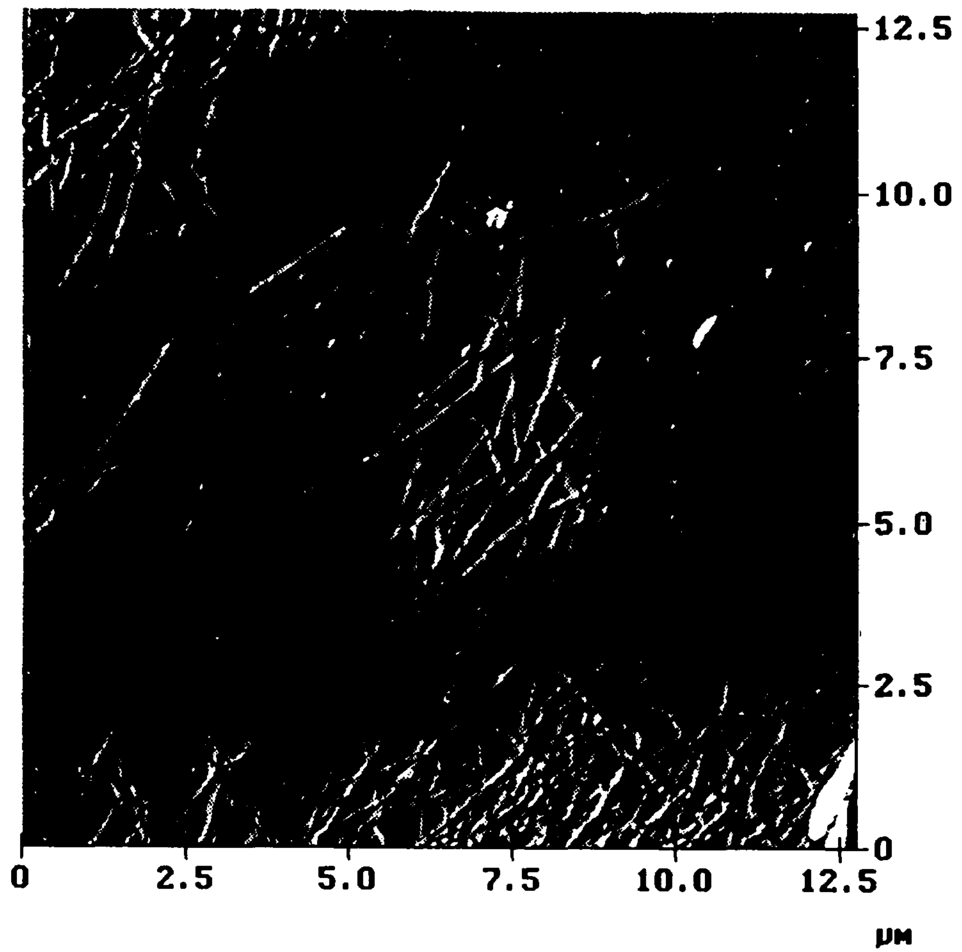
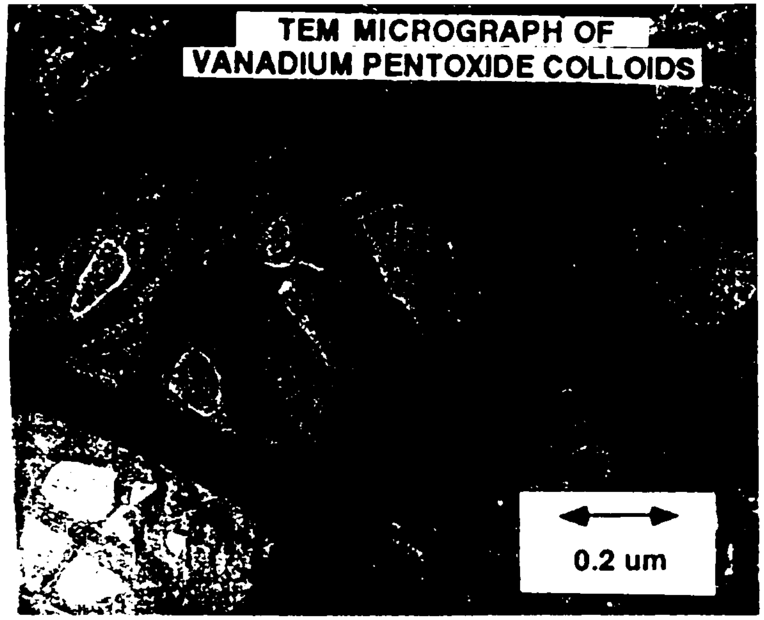
TRANSITION METAL OXIDE XEROGELS: STRUCTURE STUDIES USING ATOMIC FORCE MICROSCOPY



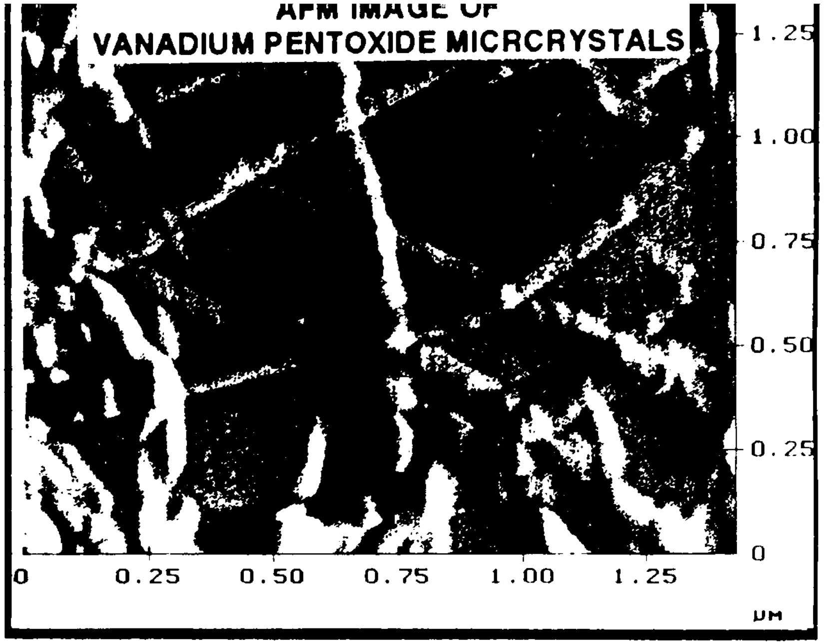
Xerogel Coated onto Glass



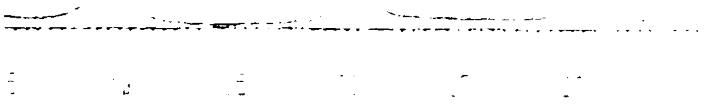
Microcrystals of Vanadium Pentoxide



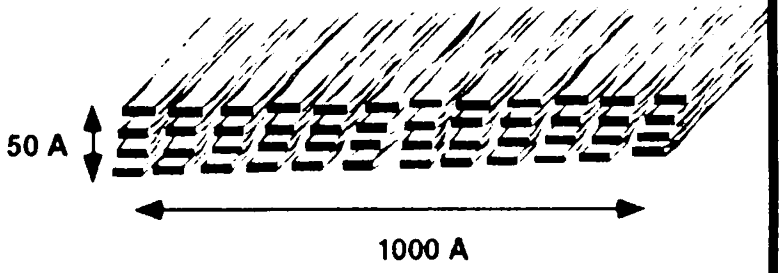
TEM MICROGRAPH OF
VANADIUM PENTOXIDE COLLOIDS



AFM IMAGE OF
VANADIUM PENTOXIDE MICRCRYSTALS



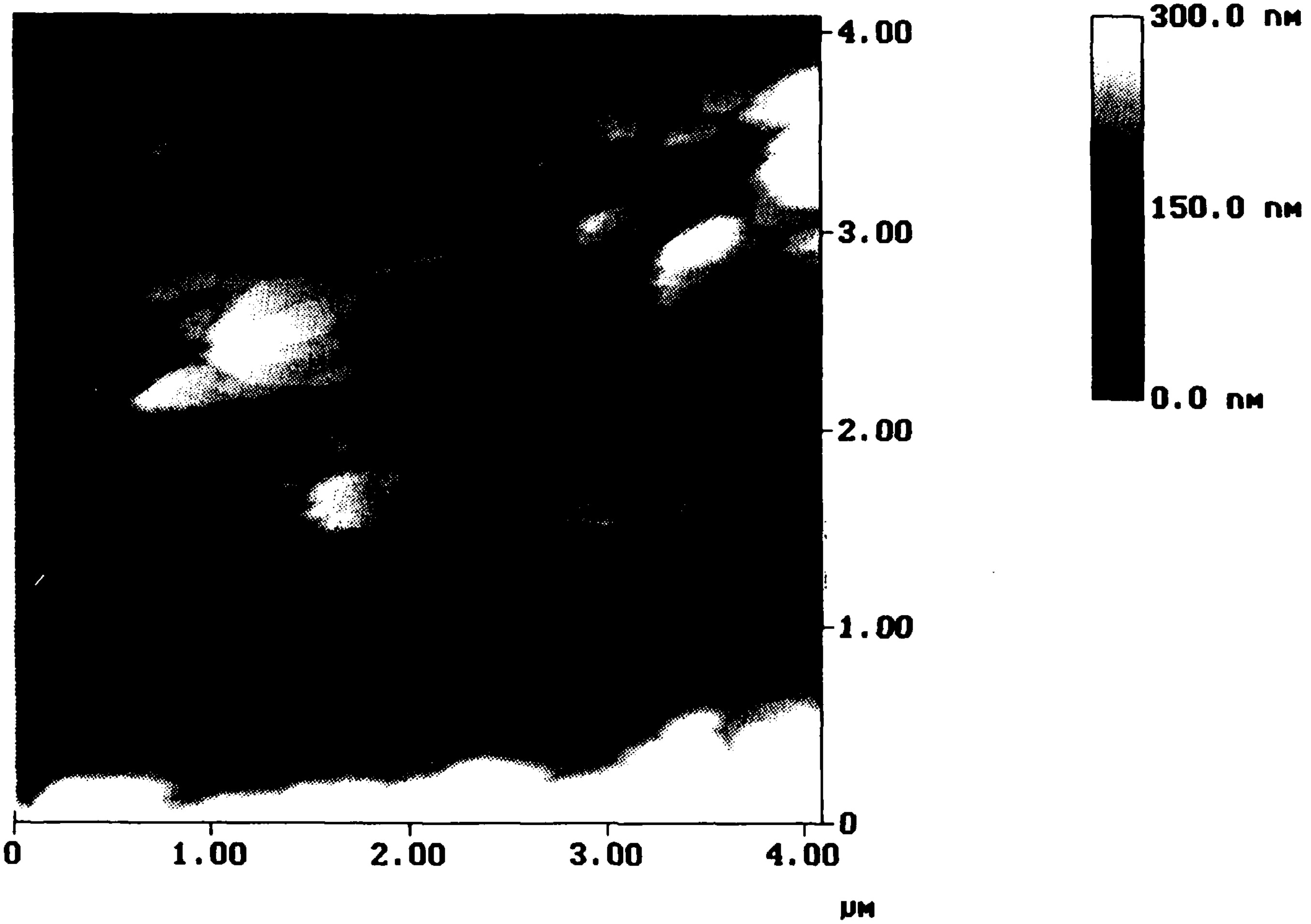
X-RAY DIFFRACTION PATTERN OF
DEHYDRATED VANADIUM PENTOXIDE XEROGEL



VANADIUM PENTOXIDE MICROCRYSTAL

0.2

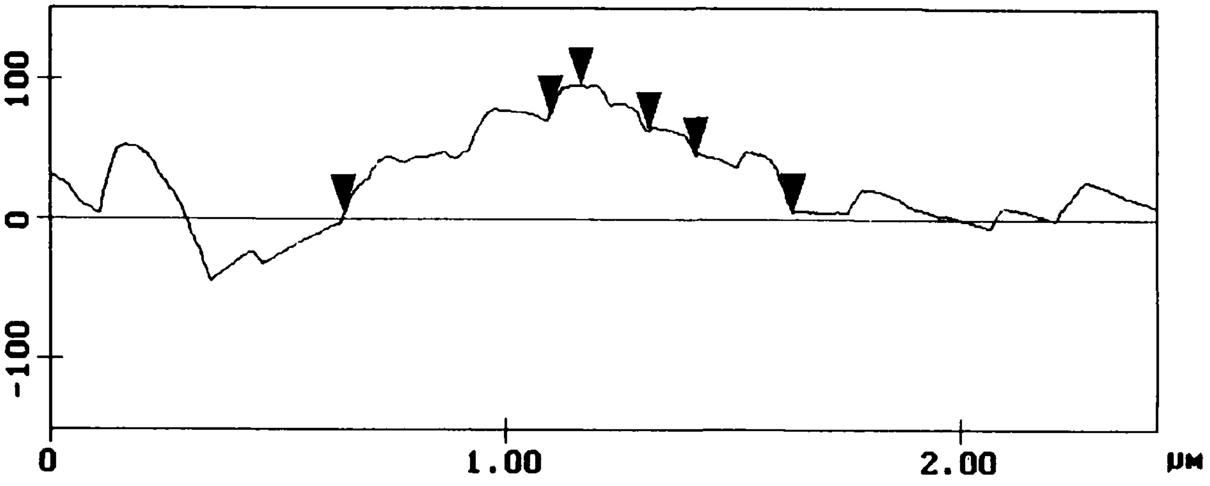
Height Angle



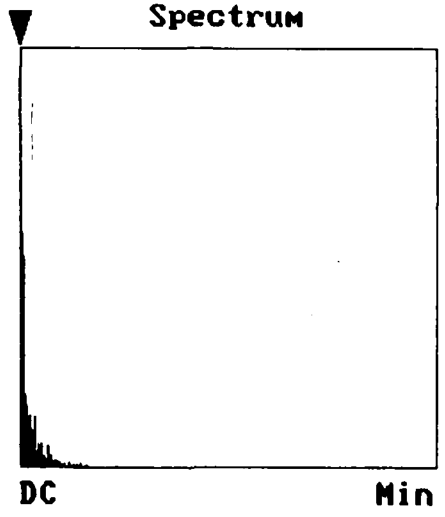
TUNGSTEN OXIDE DISCS

Height

Section Analysis



L	0.991 µm
RMS	21.814 nm
lc	DC
Ra(lc)	18.746 nm
Rmax	91.789 nm
Rz	91.789 nm
Rz Cnt	2



Horiz distance(L)	0.068 µm
Vert distance	19.791 nm
Angle	16.228 deg
Horiz distance	0.104 µm
Vert distance	18.011 nm
Angle	9.845 deg
Horiz distance	0.991 µm
Vert distance	0.959 nm
Angle	0.055 deg
Spectral period	DC
Spectral freq	0.000 Hz
Spectral amp	39.234 nm

Fixed line   Zoom 2:1   Center line Off