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Engineered Porous Materials EXPO '93

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ENGINEERED POROUS MATERIALS EXPO '93

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Abstract

This report contains a summary of the Engineered Porous Materials EXPO '93, held May 4-6, 1993 in Albuquerque, NM. The EXPO was organized to increase communication between US industry and the Department of Energy's National Laboratories. The report contains copies of viewgraphs of all speakers and reports of workshops designed to identify priority needs of industry. A conference synopsis and set of recommendations to the Department of Energy is also included.

November 1993

MASTER

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Acknowledgment:

The Engineered Porous Materials EXPO was designed to provide maximum information transfer in minimum time. The compact schedule required skilled conference coordination. The EXPO committee is indebted to Barbara Pongranz, EXPO Coordinator, who provided that skill. She assured the success of the conference through attention to detail, anticipation of problems and constant alertness. We thank Bruce Lundberg who designed the automated registration and mailing systems. We also thank Anna M. Trujillo, who not only provided tireless administrative support, but also served as conference troubleshooter. The EXPO Committee is grateful to David Julian and Anna M. Trujillo for organization and publication of this report.

The EXPO was conceived by Alan Sylwester, Denise Swink and Charles Sorrell. These individuals recognized the importance of porous materials to emerging technologies. They also recognized the need to bring together scientists and engineers from industry, DOE laboratories and universities to assure efficient utilization of the nation's skills in the materials science of porous media.

Financial support for the EXPO was provided by the Department of Energy, Office of Industrial Technology, Advanced Industrial Concepts Division. The work performed at Sandia National Laboratories is supported by the U. S. Department of Energy under contract DE-AC04-94AL85000.

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EXPO Summary and Recommendations

Engineered Porous Materials EXPO '93

Summary

The Engineered Porous Materials EXPO, held in Albuquerque, NM, May 4-6, 1993, was conceived to establish communication between government, universities and industry to foster multiple-use technologies based on porous materials. This miniconference was attended by 100 industrial scientists along with equal representation from the National Laboratories and Universities. The EXPO was sponsored by the Department of Energy (DOE) Office of Industrial Technology (OIT), the University of New Mexico (UNM), Los Alamos National Laboratory (LANL) and Sandia National Laboratories (SNL).

Porous materials are well known to the consumer, particularly for packaging. In the process and manufacturing industries, however, technologies based on porous materials have not reached their potential. In the process industries, for example, DOE studies show that 2.5×10^{15} BTU (3 % of US total consumption) of energy per year are used to separate primary products. To separate liquids, distillation typically requires 15 times the thermodynamic minimum energy. Membrane processes, on the other hand, can approach the thermodynamic limit. In spite of this potential energy advantage, membranes have made little penetration into the chemical process industries. The EXPO sought to expose recent advances in porosity engineering that could engender new technologies to harvest such unrealized energy savings.

New Mexico Senator Jeff Bingaman was invited to speak at the conference banquet. Due to scheduling conflicts, however, Bingaman was unable to attend. His speech was read by Prof. Doug Smith (UNM). Bingaman described the defense conversion and the importance of cooperative research on national economic competitiveness.

Bingaman's theme was echoed by luncheon speaker, Kay Adams, Director of the Industrial Partnership Center at LANL. She discussed the new mission of the National Laboratories under the title "Working With the National Laboratories."

Charles Sorrell, manager of the OIT's Advanced Industrial Materials (AIM) Program, lead the invited speaker program. Sorrell stressed the role of "enabling materials" in economic competitiveness. He views AIM's role as identifying key areas where DOE-funded materials R & D can seed important new technologies.

Dr. John Short (JCP Company) presented revealing analysis of the uncertainties faced by membrane developers. He surmised that the average raw materials order was only \$40,000, too small to affect the availability of needed raw stocks. As an

Fig. 1 An example of an emulsion foam presented at the poster session by William Even (SNL).

Fig. 2. Microporous foams where the cell size is controlled by the ratio of solvent to nonsolvent in the solution precursor (James Aubert, SNL). This ratio is varied so that in system a), solvent freezing quenches the structure at an earlier stage of phase separation compared to system b).

example, Short noted that Dynel, a copolymer, was superseded in the carpet fiber market and discontinued. This material, however, was the basis for very successful ultrafilters produced by Amicon and Romicon. Short's analysis led to a "catch 22." Large markets are required to guarantee specialty materials at reasonable costs. The needed markets, however, cannot be developed without consistent supplies of specialty materials.

Dr. Vinay Goel described Millipore Corporation's activities in "high-value" separations. In life science research, bioseparations, chromatography, and microelectronics, porous materials do not face in-place competing technologies. Porous materials for these specialty separations enjoy wide acceptance and represent a growth technology. Goel noted that essentially every step in microelectronics manufacturing relies on separations ranging from particulates to gases. Goel also outlined the technical challenges in high-value separations. Most of the challenges related to the engineered design of the porous media itself.

Gas separations based on zeolites, ceramics and carbon were reviewed by Charles Coe (Air Products) and Phil Hsieh (Alcoa). Coe explained that strategies for separation can follow from thermodynamic and kinetic principles. Zeolites, for example, are polycrystalline aluminosilicates that separate on thermodynamic principles. By changing the cation ratio, adsorption selectivity ratios as high as 10 can be achieved for specific pairs of gases. By contrast, amorphous materials such as carbon molecular sieves separate because of differences in permeation. This kinetic process requires designed porosity on a scale comparable to the molecular size of the target gases.

Phil Hsieh considered macrodesign issues such as the engineering of efficient membrane modules. Provision for regular backflushing is essential to both short-term efficiency and elimination of long-term fouling.

Dave Weitz (Exxon Research and Engineering Co.) discussed the impact of complex fluids in the petrochemical industry. He and his coworkers have developed a light scattering method (diffusing-wave spectroscopy) to study relaxation phenomena in aqueous foam. Weitz measured the time dependence of the foam bubble size and showed that the late-time coarsening was due to a process analogous to Ostwald ripening.

Speakers from the National Laboratories delineated strategies for the design of porosity. Using powerful analysis methods, they identified the chemical and physical processes active in processing and showed how these processes could be manipulated to achieve structural goals.

James Aubert (SNL) and Paul Apen (LANL) outlined structural control in microporous organic foams. Apen showed that emulsion-derived foams could be prepared with tailorable pore size, density, and fenestration. This flexibility is achieved by varying the monomer, oil/water ratio, surfactant and processing conditions. An example of an emulsion foam (presented by Bill Even, SNL, in the poster session) is shown in Fig. 1. In addition to tailorability, Apen noted that emulsion processing is water-based and therefore offers environmental advantages over processes based on organic solvents.

Aubert described research based on thermally induced phase separation. Competing processes such as solvent freezing, polymer nucleation, solvent nucleation and spinodal decomposition can be manipulated to generate a range of pore structures in the size range between 0.1 and 10 micrometers. Fig. 2, for example, shows polystyrene foams derived from a mixed solvent system in which the ratio of the critical temperature (T_c) and freezing temperature (T_f) is varied. When T_f is only slightly below T_c , submicron porosity is achieved (Fig. 2b). Aubert described applications of microporous foams to methane storage, battery electrodes, bioregeneration (Fig. 3), filtration

Fig. 3 Endothelial cell attached to microporous foam. (Paul Mann, UNM).

Fig. 4. A transmission electron micrograph of a nanoporous organic aerogel based on the polymerization of resorcinol and formaldehyde. (Richard Fekala, LLNL).

and interlayer dielectrics for microelectronics.

Richard Pekala (Lawrence Livermore National Laboratory, LLNL), and Dale Schaefer (SNL) discussed aerogels with pores in the nanometer range (Fig. 4). Pekala described the properties of organic aerogels which he invented in 1987. Like their foam counterparts described above, the structure of aerogels can also be manipulated through precursor chemistry and processing, leading to a range of pore sizes and properties.

Pekala reviewed the novel properties of aerogels. Aerogels offer the highest insulation (see Fig. 5) capacity of any material. In addition, due to their ultra low density (as low as 0.005 g/cm^3 , about three times the density of air), sound velocities as low as 20 m/s are realized. Finally, surface areas exceeding $1000 \text{ m}^2/\text{g}$ are common. When organic aerogels are pyrolyzed to partially graphitic carbon, they retain their porosity and become ideal materials for battery electrodes and ultra high capacity dielectrics for "aerocapacitors," capacitors with carbon aerogel dielectrics.

Dale Schaefer (SNL) examined the structure of both organic and inorganic aerogels. This lecture demonstrated the value of DOE neutron and x-ray scattering facilities for characterizing submicron porosity. From an analysis of scattering data, Schaefer showed that unusual fractal porosity could be achieved in silica-based aerogels. For organic aerogels, however, fractal structures are not observed. Here, cross-linking induces incompatibility and microphase separation leading to colloidal or particulate-like structures. In either case, the morphology of the porous solid can be tailored through the precursor solution chemistry.

Alan Hurd (SNL) described the physical processes active in the deposition of porous films. He noted that porous films are useful for devices that employ large interfacial area. Specifically, he cited a solar cell developed in Switzerland that relies on a porous titania film to obtain a thousand-fold increase in interfacial area between the titania electrode, a photoactive dye and the regenerative electrolyte.

Professor Doug Smith, University of New Mexico, reviewed the techniques available for characterization of porosity. In addition to traditional gas adsorption methods, Smith illustrated an array of other techniques available at UNM. Smith's comments caught the attention of industrial participants who repeatedly stressed the need for greater accessibility to advanced instrumentation (see below). Porous material de-

Fig. 5. Dependence of thermal conductivity on density for porous materials. Evacuated organic aerogels (RF) offer the greatest thermal resistance of any material. PX and PU are conventional foams, whereas silica and RF are respectively inorganic and organic aerogels. The minimum for the RF materials corresponds to an R/inch value of about 20, five times that of fiberglass. The abscissa is the ratio of the density of the porous material compared to the fully dense counterpart (Rick Pekala, LLNL)

velopment is dominated by small firms whose primary characterization tools are optical microscopy and nitrogen adsorption. Most small enterprises do not even have ready access to electron microscopy.

The need for better access to DOE instruments was reiterated by many of the eleven workshops that met on the second day of the conference. The workshops were commissioned to identify materials needs in particular theme areas (batteries, fuel cells, insulation, foams, catalysts, mechanics and rheology, gas storage and adsorbents, ion exchange, sensors, and environmental materials). Details of the workshop recommendations are bound in this conference report. Several common themes, however, were evident.

The workshop groups observed that skills, materials and characterization tools available to the national laboratories are not readily available to industry. For most attendees, the EXPO was their first opportunity to learn of DOE assets and accomplishments. Participants urged more systematic processes to open DOE resources to the private sector.

Several workshops noted the delays and overhead required to use the current Cooperative Research and Development Agreements (CRADAs) to formalize joint projects with the national laboratories. Small firms, in particular, felt the system was of little use to them since they lacked the staff necessary to plow through the requirements.

Most participants also felt that the National Laboratories should concentrate on the front end of the development process. With diminishing applied research in industrial laboratories, the skills necessary to “engineer” porosity are fading. Bringing porous materials to their full economic potential will require innovative research to design materials and systems with sufficient performance advantage to displace less efficient but “paid for” technologies. Every workshop noted the need to design specific pore structure and selectivity to meet the requirements for their technology.

Denise Swink, Associate Deputy Assistant Secretary of the Department of Energy (DOE) Office of Industrial Technology, closed the conference with an admonition to follow-up on the opportunities that had been “exposed” by the EXPO. She noted that a “valley of death” lies between innovative concepts and deployment of marketable technology. The DOE Office of Industrial Technology is seeking to bridge this valley through funding of cooperative projects that promise success in the private sector. Swink cited specific provisions of the Energy Policy Act of 1992 to support this new role for the OIT.

The EXPO workshop seemed to fulfill a need for both inter- and intramural communication between industry, universities and laboratories. The de-emphasis on the traditional solicitation of industry priorities was justified based on the need expressed by industrial participants for technical information of DOE capabilities. Government does not fulfill its responsibility to respond to industry by simply soliciting input, but by developing a user friendly, fair system to make its technical assets available.

Directions for the Future

It is clear that there are widespread dual-use technologies that require designed porosity. Many of the areas promising the quickest economic benefit have already been

identified. These include batteries, capacitors and low-dielectric constant interlayer dielectrics. In other cases, technical opportunities seem to have been missed.

Use of aerogels for high performance thermal insulators is an example of an enabling material that is stalled in the valley of death identified by Denise Swink. The next generation glazing and refrigeration insulators will almost certainly be nanoporous materials. Aerogels, both organic and inorganic, are promising candidates that need to be pushed through the valley. Specific synthesis and processing limitations can be overcome. The most critical limitation, the need for supercritical extraction, has already been eliminated by a UNM/SNL team. Other limitations such as brittleness, cost, and degradation can be engineered out. Use of such high efficiency insulation in refrigerators and freezers alone could save over 1% of the nations total energy usage.

Porous materials for catalyst supports and catalytic membranes offer the highest potential for economic impact. New catalysts can be inserted into existing reactors without excessive capital investment. The catalyst workshop pointed out that catalyst-dependent products account for 20% of the US GNP and a \$180 Billion export market. The \$2.1 billion catalysts business supports petroleum refining (35%), chemical processing (31%) and environmental applications (34%).

Displacement of distillation by membranes offers the greatest potential energy savings. DOE studies, however, predict that replacement of existing distillation columns with membranes is unlikely due to the high capital costs and the low cost of natural gas in the gulf coast industrial belt. In spite of these realities, separations were once again recognized as a top priority. It is interesting to note that the National Advanced Manufacturing Technologies Workshop, held in July, 1993, came to the same conclusion.

Emerging separation requirements will not be met by distillation regardless of apparent economic advantage. New commodity chemicals are likely to be of high molecular weight with corresponding high boiling temperatures. To purify these materials, new separation methods will be needed. Designed porosity in the 10-50 Å regime is essential to these emerging separation requirements. Application of nanophase technology, already perfected for bulk aerogels, to thin films offers a route to the required porosity.

Porous materials that serve as both catalyst supports and membrane separators promise the greatest impact on the chemical process industry. Such materials open routes to reaction-path selectivity beyond simple removal of product. Development of enabling materials for reactive membranes is a credible strategic goal for the OIT.

Several DOE workshops have identified the need for better access to DOE facilities for materials characterization. Laboratories such as Oak Ridge National Laboratory maintain extensive scattering instrumentation, as well as adsorption and permeation equipment. The latter is part of the K-25 Gaseous Diffusion Plant, once used to separate uranium isotopes. These existing facilities, along with new facilities such as the Advanced Neutron Source, could be configured to open needed characterization tools to industry.

Strategic Opportunities for Defense Programs Related to Porous Materials

Introduction

Over the last decade, the Department of Energy (DOE) Office of Defense Programs (DP) has supported basic and applied research on engineered porous materials. Complimentary efforts exist in DOE Energy Programs. The capability to develop and manufacture porous materials spans the DOE complex, making "engineered porous materials" a core competency of DOE.

Given its integrated strength in engineered porous materials, DOE has the opportunity to partner with industry through an integrated porous materials research and development program. The purpose of this document is to identify the strategic opportunities that warrant such a program and to outline the salient program elements.

Porous Materials in Defense Programs

From its inception, the Nuclear Weapons Program has specified, developed and fabricated porous materials. Key accomplishments include membranes for isotope separation, rigid foams for encapsulants, aqueous foams for access denial, and microporous foams for accelerator targets. The combined staff of the DOE defense complex now has the ability to engineer porosity with sizes ranging from 5 Å to 1 mm. Materials have been fabricated from all classes of materials, with densities ranging from 0.005 to 1.0 gm/cm³. These engineered materials offer a range of mechanical, adsorptive and electrical properties that have spawned new research efforts, including materials for waste clean up by the Office of Environmental Restoration and Waste Management (ERWM).

Porous Materials in Energy Programs

Starting with the development of reverse osmosis membranes by the Office of Saline Water, DOE Energy Programs have repeatedly identified porous materials as critical to energy production, utilization and conservation. The Office of Energy Efficiency and Renewable Energy (EE) is currently developing porous materials for catalyst supports, efficient insulators and chemical separations. The Office of Fossil Energy (FE) has programs in particulate and gas separation. Energy Research (ER) supports basic studies on precursors to porous materials.

Economic Impact of Improved Porous Materials

Several studies have identified the potential impact of improved porous materials. A 1991 DOE study showed that membranes could save 15% of the 2.5×10^{15} BTU of energy consumed in the chemical process industry. Development of insulating glazing materials could save every home owner \$50/per year in heating and cooling costs. Use of nanoporous insulators in refrigerators would save the equivalent of 140 supertankers of oil per year, 1 % of the total US energy budget. In the transportation industry, every pound eliminated by foams saves 30,000 barrels of oil per day in the US alone as well as 4 million tons of CO₂ emissions per year.

Engineered porous materials would enable new technologies, leading to both jobs and exports. A porous medium for hydrogen storage, for example, coupled with new fuel cell electrodes, would make the "hydrogen economy" technologically viable.

Artificial enzymes based on porous materials with "molecular recognition" could revolutionize the chemical process industry through improvement of catalytic reactions and elimination of detrimental byproducts. Finally, new commodity chemicals will require separation technologies based on porous materials with pore sizes below 100 Å. The first nation to commercialize such materials will dominate emerging commodity chemical markets, retaining domestic manufacturing jobs.

Separations are critical to both environmental cleanup and environmentally friendly manufacturing. Efficient methods to separate and recycle industrial chemicals would revitalize industries that have moved to foreign countries to avoid environmental regulation. The well-publicized cleanup problems in the DOE require efficient separation methods at almost every site. Development of requisite separation technologies awaits engineered adsorbents, membranes and filters.

The elimination of unwanted porosity is a complimentary goal of porous materials research. Pore-free ceramics would enable a host of new technologies. The ceramic engine, for example, is dependent on improved processing methods, including efficient elimination of pores during sintering. Similar defects in refractory coatings limit the use of ceramics as wear and corrosion resistant coatings.

In May 1993, a DOE-sponsored workshop on engineered porous materials identified emerging opportunities for engineered porous materials in the industrial sector. These opportunities included:

1. High efficiency gas separation membranes;
2. Catalytic membranes for chemical processing;
3. Porous electronic substrates for high speed electronics;
4. Precursors for optical communications;
5. High efficiency thermal insulators;
6. Porous electrodes for fuel cells;
7. Separators and electrodes for batteries;
8. Materials for storage of fuels including natural gas and hydrogen;
9. Selective absorbents for environmental cleanup;
10. High temperature particulate (HEPA-type) filters.

Because of the overlap of industrial and DOE requirements, workshop participants urged partnering between DOE and industrial laboratories to develop new porous materials designed to meet specific needs.

Crosscutting R & D issues

Although substantial progress has been made in the design of porous materials, numerous challenges remain. Examples include:

1. Engineered porosity below 1 µm;
2. Development of cellular metals;
3. Modeling of mechanical properties;
4. Optimization of structure for mechanical strength and toughness;
5. Continuous processing methods for micro- and nanoporous materials;
6. Molecular recognition methodologies;
7. Chemically specific absorbents;
8. Combined catalytic activity and size selectivity;
9. Ceramic precursors that sinter to pore-free monoliths;
10. Defect-free refractory coatings;
11. Tunable drainage in aqueous foams;

12. Integral defouling methods.

Breakthrough in any of these categories would affect many of the multiple-use technologies identified previously.

Program Integration

Because of the crosscutting needs for porous materials within the DOE, an integrated research program should be developed between ER, DP, FE and EE. Although broad areas of overlap exist, specific issues concern these agencies differently. These differentiating elements provide a framework for integration.

Technology Transfer Initiative: DP has traditionally supported basic and applied research in porous materials. In an era of declining research capability in industry, DP can provide the applied research base required by industry to effectively compete in new technologies. Given the corresponding decline in DP tech base funding, it is essential that some agency within DP assume responsibility to maintain the research skills needed to develop advanced materials. To fulfill this role, the Technology Transfer Division should solicit joint programs that specifically address the crosscutting R & D issues identified above.

DP research and development should target materials that impact DP-specific dual-use technologies including:

1. Battery materials;
2. Membranes for gas separation;
3. Specific absorbents for environmental cleanup;
4. High efficiency capacitor materials;
5. Low-dielectric constant materials;
6. Structural foams for lightweight vehicles;
7. Recyclable filters;
8. Porous metals.

Office of Environmental Restoration and Waste Management: ERWM has site-specific needs for absorbents and selective membranes. ERWM should partner with the Chemical Industry to develop innovative separation methods as well as environmentally benign chemical processes.

Office of Energy Research: ER should support the development of innovative ideas for separations. The deployment of membrane separation methods is hampered by the trade off between flux and selectivity. New separation concepts are needed to revitalize membrane development. Porous materials, designed at the molecular level, are needed, including nanoporous materials, artificial enzymes and smart materials (environmentally responsive, field responsive, self healing, self defouling, etc.).

Energy Research has untapped capability in synthesis, processing, and characterization that needs to be effectively coupled to application-specific programs. In addition, ER maintains numerous national facilities that should play a larger role in the synthesis, modification and characterization of porous materials. Thin film synthesis is a specific strength of ER that could be augmented to support porous materials development.

New concepts are needed to increase the efficiency of chemical synthesis through selective membranes. In addition to increasing efficiency by removal of product, selective membranes can bias chemical reactions to produce new products.

Office of Energy Efficiency and Renewable Energy: The mission of EE is currently defined by the degree to which industrial, transportation and consumer sectors utilize energy. Numerous technologies being developed by EE require engineered porous materials including:

1. Catalytic separators to enhance efficiency in the chemical process industry;
2. High efficiency thermal insulators;
3. Hydrogen and methane storage materials for hybrid vehicles;
4. Electrodes and separators for fuel cells and batteries;
5. Aqueous foams to reduce water consumption in the chemical and paper industries;
6. Porous films for energy conversion (solar cells, catalyst supports).

Office of Fossil Energy: FE has special requirements for high temperature materials. High temperature particulate filters and gas separation membranes are recognized needs. In addition, pore-free ceramic coating is critical to petroleum production, as well as coal utilization. This neglected aspect of porous materials warrants basic studies on deposition and sintering of refractory materials.

Presentation Viewgraphs

**INDUSTRIAL
REQUIREMENTS
FOR
POROUS
MATERIALS**

J o h n L . S h o r t

POROUS MATERIALS AS COMPONENTS

**An expanded PTFE membrane as part of a
"breathable" piece of outerware.**

**An ultrafiltration membrane cast on a nonwoven
polyester reinforcement, a feed spacer, and a "tricot"
weave cloth permeate carrier, as components of a
spiral wound module, itself part of a system for
concentrating the fat and protein in milk, operating in
a Dairy.**

**A hollow fine fiber reverse osmosis membrane, in a
module as part of a seawater desalinization system,
in the Middle East.**

**A gas separation membrane in a module in an
atmospheric gas separation system for "Nitrogen
blanketing" in the CPI**

MANUFACTURERS REQUIREMENTS

Availability

Price

Variability - batch to batch

Ability to QC

**Capital requirements
equipment
special precautions**

Scrap minimization

Process automation

**Storage stability
raw material
finished product**

Regulatory compliance

**"Cradle to grave"
responsibilities**

RAW MATERIALS

Long term availability

"Dynel", a copolymer of PVC and PAN, was superceded in the market for carpet fibers and was discontinued, it was also however, the basis for a very successful hollow fiber ultrafilter from Amicon and Romicon.

ICI, the major, and virtually sole supplier for Polyethersulfone, decided that it did not have a large enough market as an engineering plastic to justify it's continuing production. It was also the basis of a differentiated ultrafiltration membrane used extensively in the Dairy market.

**Porous
materials are
generally not
used in large
enough
volume to have
a significant
influence over
raw material
price and
availability**

INTERNATIONAL MEMBRANE SALES ESTIMATES

POLYMERIC MICROFILTRATION

Total 1992 Sales; \$842 million

Millipore	\$400 million	47.5%
Pall	\$185 million	22.0%
Sartorius	\$ 90 million	10.7%

REVERSE OSMOSIS

Total 1992 Sales; \$184 million

Filmtec/Dow	\$ 50 million	27.2%
Hydranautics	\$ 24 million	13.0%
DuPont	\$ 20 million	10.9%
Fluid Systems	\$ 19 million	10.3%

ULTRAFILTRATION

Total 1992 Sales; \$92 million

Koch/Abcor	\$ 25 million	27.2%
Amicon	\$ 20 million	21.7%
Rhone Poulenc	\$ 10 million	10.9%
Dow Danmark	\$ 10 million	10.9%

LEVERAGE

TOTAL SALES p.a. \$ 1 billion

Average Gross Margin 50%

**Total Manufacturing cost \$ 0.5
billion**

**Materials as a percentage
approx 20%**

Total Materials cost \$ 100 million

**Membrane materials as
percentage of material cost 33%**

Number of polymers 10

Number of companies 20

Number of orders per year 4

Value of each order \$41,250

Other examples of problems include

- * Feed spacer material used in Spiral Wound modules is relatively "low tech" (potato sacks), only recently have some suppliers found membranes an interesting market, but still low volume.**
- * Most woven or nonwoven materials are used primarily in the textile market with membranes taking a small share of total output.**
- * In order to find suitable adhesives for a range of products, the most rugged may be eliminated because it is not approved for food contact by the FDA.**

Innovative way around the problem is to use an existing high volume product, such as catalytic converter as the substrate for a proprietary coating.

Disadvantage remains of little leverage over the supplier, whose specifications and requirements may change, or who may be unwilling to satisfy a small customer.

"IN USE" CRITERIA

**Chemical compatibility with
process stream**

**Chemical compatibility with
cleaning chemicals**

Thermal limits

Aging and fatigue

**Short term surface interactions,
"Concentration Polarization"**

**Long term interactions,
"Fouling"**

DISPOSAL AND/OR REUSE

**Modules operating on "clean"
streams are being rebuilt, i.e.
Reverse Osmosis desalination
modules.**

**Some components pose
disposal problems e.g. PVC in
Europe.**

**The number of different plastics
involved in a Spiral module,
(polypropylene, polyester,
polysulfone, etc) makes
recycling difficult.**

**"Used" modules may contain
hazardous or harmful materials,
(Lead from automotive primer
paint, biohazards from
pharmaceutical processes, etc)**

Overview of Microporous Materials for Gas Separation

Charles G. Coe

Corporate Science and Technology Center
Air Products and Chemicals, Inc.
7201 Hamilton Blvd., Allentown, PA 18195-1501

For over 25 years microporous materials have been the heart of commercial adsorptive separation processes. Recent advances in adsorbent development have been important to improving gas separation processes as well as providing the cornerstone for completely new processes. Adsorptive separation processes are projected to be an important unit operation to address environmentally important separations such as recovering methane from landfills or CO₂ from enhanced oil recovery. Adsorbent properties and the process must be carefully matched to provide optimum performance.

The structural variability of microporous adsorbents provides a means for controlling the equilibrium and kinetic adsorption parameters over a wide range. Specific structural features can be combined to provide materials having adsorption. After giving an overview of adsorptive processes, results from the development of adsorbents for producing oxygen and nitrogen from air will be given to illustrate the importance of molecular structure on selectivity, gas capacity, and uptake rates. The examples given are applicable to a range of gas separation problems and demonstrate important principles to consider in designing adsorbents. Zeolitic adsorbents are used to produce oxygen and operate under equilibrium condition. Both N₂ capacity and selectivity are strongly influenced by the type, size, location, and number of accessible cations present in zeolitic adsorbents as well as the structure type. Carbon molecular sieves (CMS) are a subgroup of activated carbon which are only mildly selective for O₂ over N₂ at equilibrium; however, the pore structure is carefully controlled to allow O₂ to adsorb 30 times faster than N₂ providing a means to produce N₂ via a kinetic based process. The overall pore structure and especially the effective micropore hydrocarbons. The ability to control the size of the micropore openings without significantly altering the rate of gas uptake is a major synthetic challenge. Molecular probe studies illustrate how changes of 0.3 Å in the effective micropore size dramatically alter the separating ability of the CMS. The relative equilibrium affinity for sorbates on carbons can also be manipulated by varying the surface composition providing another means of altering selectivity.

Of course, one can envision incorporation of these adsorbents into a membrane configuration. In microporous membranes gases can be separated by molecular sieving, knudsen diffusion, selective surface flow, or facilitated transport. Facilitated transport using an immobilized molten salt membrane containing NaNO₃ provides a method to achieve high selectivity at 500°C. Advances in membrane fabrication techniques, basic synthesis of molecular sieves, and post modification techniques will be important to the development of energy efficient separation technologies for the next century.

Overview of Microporous Materials for Gas Separation

C. G. Coe

Corporate Science and Technology Center

Air Products & Chemicals, Inc.

Engineered Porous Materials Expo '93

May 4-6, 1993

OUTLINE

- **Gas Separation Opportunities**
- **Process overview**
- **Examples**
 - Zeolites**
 - Carbons**
 - Membranes**
- **Challenges**

Materials Needs for Difficult Separations

- CH_4 / N_2 - Natural Gas Recovery
- $\text{CO}_2 / \text{CH}_4$ - Enhanced Oil Recovery
- $\text{CH}_4 / \text{CO}_2 / \text{N}_2$ - Landfills, Biogases
- $\text{SO}_x / \text{NC}_x$ - Lower emissions

Important PSA Parameters

Selectivity - Recovery

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Working capacity - Productivity

Evacuation gas - Energy

ADSORPTIVE AIR SEPARATION

EQUILIBRIUM (ZEOLITES)

KINETIC (CARBON MOLECULAR SIEVE)

REPRESENTATION OF ZEOLITE STRUCTURE

ZEOLITE A

ZEOLITE X OR Y

CATION POSITIONS IN X ZEOLITE

- INACCESSIBLE
- ACCESSIBLE

Structural Factors that Influence Adsorption

- Si/Al Ratio
- Cation siting
- Pore Size and Shape
- Intergrowths and Defects
- Crystallite Size and Aggregation

Properties of Zeolites for Air Separation (30°C, 1 atm)

Adsorbent (Si/Al)	N ₂ /O ₂ Selectivity	N ₂ Capacity [cc/g]	O ₂ Capacity [cc/g]
Ca A (1)	4.6	14	4.4
Ca X (1.2)	8.1	19	5.7
Ca LSX (1)	10.4	26	7.0

INFLUENCE OF CATION ON NITROGEN ADSORPTION OF CHABAZITE

**And Now For Something
Completely Different:**

ADSORPTION EQUILIBRIA AND ADSORPTION RATES OF OXYGEN AND NITROGEN WITH CMS

ORIGINAL
MICROPORES

"TREATED"

O_2

N_2

Molecular Probes

CH_2Cl_2

CHCl_3

i-pentane

n-butane

MICROPOROSITY OF CMS ADSORBENTS

MATCHING THE HYDROCARBON SIZE TO THE PORE SIZE

PROPYLENE /
"3 Å PORE"

HEAT

PROPYLENE /
"4 Å PORE"

HEAT

ISOBUTYLENE /
"4 Å PORE"

HEAT

Rate vs Selectivity for CMS

M. Suzuki *et. al.* 3rd Pacific Eng Conf (1983)

Membrane Separation Mechanisms

- Knudsen diffusion
- Molecular Sieving
- Selective Surface Flow
- Facilitated Transport

CMS Membranes Show Selective Permeance

Membrane	Permeability (Barrer) O ₂ N ₂	Selectivity	Separation Power
Silicone Rubber	396 184	2.15	8.3
MSC membrane	17,100 240	7.1	124

J. Koresh, *et. al.* Sep Sci &Tech (1983)

O₂ from N₂ Using IMS NaNO₃ Membrane

Temperature (°C)	Permeability P_{O_2} ¹ (barrer)	Selectivity ² $S = P_{O_2}/P_{N_2}$
452	58	4
477	172	12
500	439	31
525	1110	79

¹The thickness of the membrane is taken to be 0.02 cm.

²The nitrogen permeability, P_{N_2} remained relatively constant at 12–15 barrer.

G. P. Pez, *et. al. J Membrane Sci.* **1992**, 65 21-30.

Challenges

- Adsorbents
 - selectivity for minor component
 - balancing selectivity and rate
 - high volumetric capacity
 - good reversibility for PSA
- Membranes
 - high selective permeance
 - dimensional stability under process conditions
 - viable fabrication methods

Porous Materials Requirements for High Value - Added Separations

**Dr. Vinay Goel
Millipore Corporation**

Separations is a loosely defined term which includes analysis and purification of fluids. It is roughly a 4 billion dollar industry today. Millipore is a key player in this high value-added separations industry with its two major technologies - membranes and chromatography.

Membranes and chromatographic processes are gaining wide acceptance in microelectronics, pharmaceutical, bioprocessing, and life science research applications. As these industries advance, their needs are becoming increasingly specialized and demanding. Higher performance levels and better cost effectiveness will be required from new porous media being developed for these applications. Environmental considerations will restrict the degrees of freedom available in choice of materials.

Porous Materials Requirements for High Value-Added Separations

Vinay Goel
Vice President, Membrane Research
Millipore Corporation
Bedford, MA

Outline

- Definitions
- Millipore technologies
- Markets of interest
- Specific applications within markets
- Future needs and challenges

Definition of Separations

Separations is a loosely defined term which includes analysis and purification of fluids

Definition

- Analytical products are used to gain knowledge about a sample by detecting, identifying and or quantifying its chemical, physical or biological components.

Definition

- Purification products are used to help manufacture or process a customer's product by removing contaminants or by isolating and purifying specific components from complex mixtures

Separations Industry - By Technology

Total \$3.2 billion in 1990

Millipore sales can be looked at based on our different technology segments

Membranes help to separate samples into their different components

Chromatography separates samples into their various components

Capillary Electrophoresis separates a sample into its components

Ions placed in the capillary will move according to their "mobility" in relation to the applied charge.

Cross Section of Capillary Filled with Electrolyte

Microelectronics Applications

Filtration and purification of:

- DI water
- Chemicals
- Photo chemicals
- Gases

Our technology needed at each stage

Separations Processes Used

- Coarse filtration
- Membrane microfiltration
- Membrane ultrafiltration
- Reverse osmosis
- Ion exchange
- Reactive resins
- Molecular sieves

Millipore is involved in many stages of Pharm/Bio processing

On line Monitoring

Quality Control

Cell Harvesting

Purification

Concentration

Sterilization
Depyrogenation

Sterile Filtration
Air Water Media

Quality Testing

Pharmaceutical/BioProcessing Applications

- Clarification/coarse filtration
- Bioburden reduction
- Sterile filtration-gases and liquids
- Cell harvesting
- Cell lysate processing
- Protein separation
- Protein concentration
- Depyrogenation
- Virus removal

Analytical Applications

- Microbiological analysis
- Particulate analysis
- Cell biology
- Protein separation
- Protein and nucleic acid blotting
- Protein and nucleic acid sequencing

Millipore brings the broadest range of technology to life science research

Separations Technologies Used

- Microporous membranes as collection screens
- Microporous membranes as adsorptive substrates
- Microporous membranes as transport vehicles
- Gel electrophoresis
- Chromatography
- Bioinstrumentation

Challenges and Future Needs ***Microelectronics***

- Removal of finer and finer particles at current throughputs
- Removal of dissolved ions from chemicals
- Removal of trace impurities from gases
- Cleanliness measures moving from ppb to ppt
- Environmentally-safe materials and processes

Challenges and Future Needs Pharmaceutical/Bioprocessing

- Absolute removal of viruses from recombinant proteins
- Faster chromatographic separations
- Validated function
- Non-interactive porous media
- Environmentally-safe materials and processes

Challenges and Future Needs Analytical Applications

- Micron to micron uniformity of structure and surface chemistry
- Switchable surface chemistries
- Ability to handle smaller and smaller sample sizes
- No fluorescence background materials
- No non-specific protein binding
- No non-specific nucleic acid binding
- Environmentally-safe materials and processes

Conclusions

- Needs are becoming more and more application-specific and specialized
- Inertness, non-interactiveness and cleanliness standards for materials are being pushed to new limits constantly
- Microuniformity is becoming more important
- Environmental considerations are dictating more of the choices

ORGANIC AEROGELS: AN UPDATE ON PROPERTIES AND POTENTIAL APPLICATIONS

Richard W. Pekala

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Aerogels are a special class of foams

- **Nanostructure**
 - open cell, continuous porosity
 - ultrafine cell/pore size (< 100 nm)
 - interconnected particles (diameter ~ 10 nm)
 - high surface areas (400-1100 sq.m./g)
 - wide range of densities (0.01-1.0 g/cc)
- **Chemical Composition**
 - synthesized from metal alkoxides or selected organic monomers
 - sol-gel mechanism
- **Drying procedure**
 - supercritical extraction

Generic sol-gel polymerization

(i)

Reactants

(ii)

Clusters
3-20 nm

(iii)

Gel

**SOLUTION CHEMISTRY DETERMINES THE MICROSTRUCTURE
OF THE FINAL AEROGEL**

Structural model

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Requirements for organic sol-gel polymerizations

- **Multifunctional monomers**
- **High degree of crosslinking**
- **Surface functional groups**
- **Particle stabilization**
 - **electrostatic**
 - **polymer / solvent interactions**

A synthetic route for the production of organic aerogels has been developed

Resorcinol

Formaldehyde

crosslinked polymer

RF gels are processed in the following manner

Stir RF mixture

Sealed vials

7 day cure

(i) acid wash
(ii) acetone exchange

Supercritical
extraction

RF aerogels

1075 °C

Carbon
aerogels

**RF aerogels are dark red in
color and transparent**

500 Å

Carbonized aerogels are easily machined

**The aerogel microstructure is
retained even after carbonization
at 1075 °C**

500 A

FM-3097-U-S6-1A

Organic aerogel microspheres

Resorcinol-formaldehyde

Carbon

Solution chemistry dictates the structure and properties of RF aerogels

High Catalyst Conditions R/C=50	Low Catalyst Conditions R/C=300
<ul style="list-style-type: none">• small particle size ~ 30 Å• high surface area ~ 900 sq.m./g• higher density .08 g/cc• polymeric; interconnected fibers• higher compressive modulus• slower NMR relaxation times	<ul style="list-style-type: none">• large particle size ~200 Å• low surface area ~ 350 sq.m./g• lower density .06 g/cc• colloidal; interconnected particles• lower compressive modulus• faster NMR relaxation times

A change in microstructure accompanies the variations in surface area

R/C = 50

500 Å

R/C = 300

500 Å

New synthetic approach to organic aerogels

• Monomer Route

• Oligomer Route

- Resimene 714 (Monsanto Chemical Co.) is acidified to form crosslinked gels
- principal reactive group $\text{-N} \begin{cases} \text{CH}_2\text{OCH}_3 \\ \text{CH}_2\text{OH} \end{cases}$

Synthetic conditions affect the surface area of MF aerogels

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Aerogel structure-property relationships

- Optical
- Thermal
- Acoustic
- Electrical
- Mechanical

Controlling structure at the nanometer scale has a dramatic effect upon the properties of porous materials

Thermal conductivity of RF aerogels

- A Guenther (1962), PU
- B Guenther (1962), PF
- C Skochdopole (1961), PS
- D Guenther (1962), PS
- E Fricke (1991), R-F
- F Fricke (1990), Silica

Radiative, gaseous, and total conductivities for R-F aerogels versus density

Thermal conductivity of evacuated aerogels

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Aerogels exhibit unusual acoustic properties

- **low density aerogels (< 0.1 g/cc) propagate sound at velocities less than in air**
- **sound velocity exhibits power-law dependence on aerogel density**
- **aerogel composition, matrix morphology, and gas pressure effect sound velocity**
- **sound velocity decreases during uniaxial compression**
- **acoustic impedance (product of bulk density and sound velocity) is smaller and spans a wider range in aerogels than in any other known material.**

Acoustic properties of aerogels

ns

Silica Aerogel

- (1) Acid Cat.
- (2) Condensed
- (3) Base Cat.

RF Aerogel

- (a) R/C= 50
- (b) R/C=200
- (c) R/C=300

CRF Aerogel

- (A) R/C= 50
- (B) R/C=200
- (C) R/C=300

(c)

Electrical conductivity of carbon aerogels as a function of temperature

Power-law dependence of electrical resistivity on bulk aerogel density

What is an Aerocapacitor?

- A high power and energy capacitor based on the voltage induced separation of charge (double layer) at an electrolyte/solid interface
- The amount of double-layer space-charge effect (capacity) scales directly with the amount of usable electrode surface area
- The Aerocapacitor uses LLNL high surface area carbon Aerogels as both the positive and negative electrodes

Density and R/C ratio of the carbon electrodes affect capacitance measurements

* Specific surface area displays an inverse relationship with the R/C ratio

Carbon aerogels are being tailored for supercapacitor applications

- pore size distribution
- surface area
- surface groups (e.g. -COOH, -OH)
- carbon structure (amorphous vs graphitic)
- electrical conductivity
- incorporation of selected metals or metal oxides

CONVERSION VS. CARBONIZATION TEMPERATURE

Compound I + carbonized resorcinol-formaldehyde

400 c, 1h, wt. ratio 9,10 DHP:l:cat 4:1:1
conversion corrected for surface area catalyst 800 m²/g

Summary

- We have demonstrated the synthesis of organic aerogels based upon the aqueous, polycondensation of (1) resorcinol / formaldehyde or (2) melamine / formaldehyde
- Organic sol-gel chemistry can be used to tailor the structure and properties of aerogels at the nanometer level
- Commonalities between organic and inorganic aerogels suggest that a universal model might be developed for the structure and properties of these unique materials
- We believe that organic sol-gel chemistry can be applied to other monomer systems and / or combined with inorganic systems to produce new materials with potentially interesting thermal, optical, and electrical properties

COMPLEX FLUIDS RESEARCH FOR INDUSTRIAL APPLICATIONS

Dave Weitz

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- **What are Complex Fluids**
- **Why are they important:**
 - **for industrial applications**
 - **for Exxon**
- **Examples of Complex Fluids Research.**
- **Modern Trends in Industrial Research**
- **Opportunities For New Partnerships**
- **Future of Complex Fluids and Porous Materials Research.**

Porous Materials Expo, Albuquerque, NM, 5/5/93

COMPLEX FLUIDS

Fluids containing structures larger than the fluid molecules

Examples:

- Microemulsions
- Surfactants
- Multiphase fluids
- Colloidal Dispersions
- Polymers
- Emulsions
- Foams

Fluids in Complex Geometries

Examples:

- Fluids in Porous Media
- Fluids in Micro-Porous Media
 - eg* catalyst supports

IMPORTANCE OF COMPLEX FLUIDS

Very wide-spread industrial uses:

Colloidal Dispersions:

paints, coatings, ceramics

Emulsions:

Coatings, cosmetics, foods, oil recovery

Foams:

Oil recovery, foods, cosmetics, insulation

Polymers:

Structural materials, additives

Surfactants:

Additives, stabilization, cleaning, cosmetics

This list is representative, not all-inclusive

IMPORTANCE TO THE OIL INDUSTRY

Virtually all fluids used in the oil industry are complex fluids

Microemulsions:

Tertiary oil recovery

Surfactants:

Additives in fuel, lubes, chemicals

Multi-phase fluids:

Oil recovery, oil refining

Colloidal Dispersions:

Drilling fluids, additives, lubes, coatings

Emulsions:

Coatings, tertiary oil recovery, refining, oil spills

Foams:

Refining, tertiary oil recovery

Fluids in Porous Media

All oil recovery

Fluids in Microporous Media

Refining, chemicals, many catalysts

This list is again representative, not all-inclusive

FOAMS

Doug Durian UCLA

Example of Complex Fluids Research

Important for several areas of porous materials

Demonstrates how basic research leads to new results of potential technological interest

Example of research driven investigation

How is research managed and directed at Exxon

Competing needs, directions

Future trends

LIQUID FOAMS

What is a foam:

- Bubbles of gas in a fluid
- Stabilized by a surfactant at the interfaces
- Typically have large volume fractions of gas

Wet foam

- Relatively large amount of fluid
- Bubbles are nearly spherical

Dry foam

- Fluid drained from structure
- Polyhedral bubbles
- Mainly surfactant films

All foams will drain, but rate can be reduced

Properties of Foams:

- Solid, with yield stress.
- But will flow with sufficient shear
- Low density, high expansion
- High surface area.

Uses (selected):

- Food, cosmetics
- Firefighting
- Oil recovery: rheological properties

Often encountered when they are not desirable

- Processing, oil spills

STABILITY OF FOAMS

Key issue for all uses:

Maintain the foam when it is desirable

Destroy the foam when it is undesirable

Two main methods for destabilization:

COALESCENCE

Films between neighboring bubbles break

Bubbles merge together

OSTWALD RIPENING

Diffusion of gas through fluid between bubbles

Driven by differences in pressure inside bubbles

Pressure controlled by Laplace pressure: σ/r

Higher in smaller bubbles than in large bubbles

Small bubbles shrink

Large bubbles grow

STABLE FOAMS: Slow destabilizing processes

Drainage slowed by increasing fluid viscosity

Coalescence decreased by using appropriate surfactant

Ostwald ripening more difficult to control

RESULT:

Foams Coarsen in time

Average bubble size increases with time

LIGHT PROPAGATION IN FOAMS

Foams are white

Large number of interfaces

Scatter light very strongly

Visualization very difficult

Light DIFFUSES through the foam

$$\frac{\partial U}{\partial t} = D_{\ell} \nabla^2 U$$

U Concentration of diffusing photons

$$D_{\ell} = \frac{c\ell^*}{3} \quad \text{Diffusion coefficient for light}$$

ℓ^* New length scale for light propagation:

Length for randomization of direction of photon

DIFFUSIVE TRANSMISSION

Expanded source: $T \approx \frac{\ell^*}{L}$

Point source: $T \approx \frac{\ell^*}{L} \frac{a^2}{L^2} \propto \frac{1}{L^3}$

MEASURE LIGHT TRANSMISSION THROUGH FOAMS

-100-

Very simple measurement:

Total transmission through foam sample of thickness, L

Compare to calibrated sample

Obtain transport mean-free path, ℓ^*

Single length scale which characterizes transmission of light through foam

—|—|—
20µm

GILLETTE FOAMY

HIGHLY REPRODUCIBLE SAMPLES

INITIAL BUBBLE SIZE $\sim 20 \mu\text{m}$.

VOLUME FRACTION OF FLUID ~ 0.08

TRANSMISSION vs. THICKNESS

$T \sim \frac{1}{L} \Rightarrow$ DIFFUSIVE TRANSMISSION

MEASURE $\rightarrow$ ℓ^*

l^* MEASURES AVERAGE BUBBLE DIAMETER

$l^* \rightarrow$ FROM STATIC TRANSMISSION

$d \rightarrow$ FROM SURFACE MEASUREMENT

$$l^* \sim 3.5 d$$

CONSISTENT WITH GEOMETRIC OPTICS
PICTURE OF SCATTERING.

SCALING BEHAVIOR IN FOAM COARSENING

FROM STATIC TRANSMISSION

$$d \sim t^{0.45}$$

MEAN FIELD THEORY FOR FOAMS:

LATE TIMES $t^{1/2}$

EARLY TIMES $t^{1/3}$

COARSENING OF FOAMS

Small bubbles shrink

Large bubbles grow

ANALOGOUS TO OSTWALD RIPENING

Early times:

Dilute:

Each sees same concentration

$$r \approx t^{1/3}$$

Late times:

Concentrated:

Diffusion across wall

Gradient established by neighbor

$$r \approx t^{1/2}$$

Identical for foams

Measured dependence: $r \approx t^{0.45}$

EVOLUTION OF FOAM RESEARCH

Driven by new developments in experimental techniques:

- Applications of multiple light scattering

Developments in multiple light scattering driven by

- Interest in the scientific community in light localization

- Needs in Exxon to measure particle size in concentrated dispersions

Developed new light scattering technique:

- Diffusing-Wave Spectroscopy

- Extends Dynamic Light Scattering to multiple scattering limit

Developed new approach to the study of strongly scattering media

DWS very useful for research studies, but

Initial technological application of DWS:

- Failure

- But: learned information that proved even more valuable

Conclusion:

- Exploit input of both technological need and basic research

- Result: good science and useful technology

Traditional model of research:

- Driven by both curiosity and technological need

Future research likely to be much more highly DIRECTED

- More tightly coupled to technological needs

FUTURE DIRECTION OF FOAM RESEARCH

Key issues:

- Stability of Foams

- Rheology of Foams

- Combine rheological measurements with light scattering

Application of Foams:

- Key application is in oil recovery

- Critical issue: Flow in porous media

- Pore size may be comparable to the bubble size

Generalize study

EMULSIONS

Similar to Foams, share many features

Liquid droplets of one fluid in a second

- Gas of Foams replaced by a second liquid

Physical properties, rheology, similar to Foams

Also frequently encountered in oil industry

- Foams for oil recovery often under high pressures

- Emulsions result rather than foams

Major advantages in the study of their properties:

- Greatly improved stability, no changes with time

- Bouyancy match: eliminate drainage

- Insoluble liquids: eliminate Ostwald ripening

- Good surfactants: eliminate coalescence

- Indefinite stability

Program: Study of Foams and Emulsions

- Stability

- Physical properties

- Light scattering

- Rheology

FUTURE TRENDS IN INDUSTRIAL RESEARCH

Amount of basic research supported by industry will decrease

Increased competition in global economy

Increased expense of research

Increasingly short term view

Research is being "downsized"

Need for research will increase:

More complex, rapidly changing technology

"Mature" industries will have to develop technology

Increased competition in global economy

Need for new research and technologies is recognized

New methods to focus research required

Must still allow basic research to flourish

Represents the future technologies

New paradigm for defining and performing basic research

New partnerships and collaborations will be essential

NEW OPPORTUNITIES

BASIC RESEARCH AT EXXON CORPORATE LAB

New model for guiding basic research

Still being carried out; Not clear what the outcome will be

Advantages:

- Strategic definition of critical science needs

- Have business units approval from the start

- May become new model for research management

Dangers

- Control and direction too tight

- Stifle creativity and basic research

NEW OPPORTUNITIES FOR COLLABORATIONS

Needs:

- Increased amount of research
- More complex questions
- New technologies

Constraints:

- More expensive to do research
- Less support for research

NEW PARADIGM

- Basic research more highly justified

LEVERAGE RESEARCH

- Collaborations with other industries
- Collaborations with universities
- Collaborations with governments labs

Systems Approach: Collaborate with other industries

Basic Research: Collaborate with universities

Complex Research: Collaborate with governments labs
Need bigger resources than single industry

TRENDS FOR RESEARCH IN THE PETROLEUM INDUSTRY

Environmental Requirements:

- Legislative and public pressure
- Reduce deleterious environmental impact of all technologies
- New opportunities for research

Requirements:

- Better understanding of environmental impact
- All new technologies will include environmental concerns
- New clean-up technologies will be developed

Biology

- Use biotechnology to do chemistry more efficiently
- Use biotechnology to assist in environmental clean-up
- Learn from biology for more efficient chemistry

COMPLEX FLUIDS:

- Critical in physics, chemistry and chemical engineering

New Opportunities for Collaborations:

- Exploit computer resources for improved modelling
- Scattering facilities for structural studies of complex fluids
- Materials expertise to design new systems
- Lab resources to fully study important systems

Example: Flow in Porous Media

- Small scale physics is better understood (but not fully)
- Scaling to field size is not understood at all

CROSSLINKED POLYSTYRENE FOAMS

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Crosslinked polystyrene foams can be prepared from high internal phase water-in-oil emulsions. Microcellular rigid crosslinked polystyrene foam is prepared by mixing water, styrene, divinylbenzene, and sorbitan monooleate (SMO) to form a high internal phase water-in-oil inverse emulsion. The SMO is an oil soluble surfactant and stabilizes the high internal water phase emulsion. The emulsion is heated to induce polymerization of the styrene monomers which closely replicate the emulsion structure. The water phase acts as the pore former during polymerization and is removed by drying. This leaves a porous rigid microcellular foam.

This presentation will focus on how foam microstructure and morphology are controlled. For example, the pore size, cell size, surface area, and openness of the foam can be Varied depending on the composition of both the oil and the water phases, the ratio of surfactant to monomer(s), the initiator, and the degree or method of mixing. Open and closed-cell polystyrene foams of density 0.02~0.200 g/cc with cell sizes ranging from 1~0 microns will be described.

We are using rigid microcellular foams for a variety of applications. Several will be briefly mentioned.

CROSSLINKED POLYSTYRENE FOAM

Paul Apen

**Acknowledgements: James Gray, Joel Williams,
Raimond Liepins, Joseph Duke and Robert Hermes**

***Polymers and Coatings Group, MST-7
Los Alamos National Laboratory***

PORE-FORMER ROUTE FROM MONOMERS

- **OBJECTIVE:**

- **A VERSATILE ROUTE TO OPEN-CELLED FOAMS**

- **CONSIDERATIONS:**

- **SIMPLE**
- **MOLDABLE / MACHINABLE**
- **LARGE SIZES**
- **SMALL CELLS**

- **APPROACH:**

EMULSION-DERIVED FOAMS

Water + **Oil**
(with surfactant)

Mix

**High Internal Phase
Water-in-Oil Emulsion**

Monomers

- *Styrene / DVB*

Surfactant

- *Sorbitan Monooleate (SMO)*

Water

- *"Pore Former"*

Initiator

- *K₂S₂O₈ or AIBN*

Mixing

- *Gear Pump, Mechanical Stirrer,
or Syringe Pump*

Additives

- *Aliphatic Hydrocarbons, Salt*

WATER-IN-OIL EMULSION COMPOSITION

MICROSTRUCTURES OF STYRENE/DIVINYLBENZENE EMULSION FOAMS

COMPRESSION OF WATER DROPLETS AS % SMO INCREASES

5%

10%

20%

WATER-IN-OIL EMULSION INTERFACE

Toroid formed by aromatic monomers around surfactant window between two surfactant-coated water droplets

EFFECT OF CONDITIONS ON FOAM MICROSTRUCTURE

	Cell Size	Pore Size	Openness
↑[Monomers]		↓	↓
↑[SMO]		↑	↑
↑Mixing/Shearing	↓	↓	
Hydrocarbons		↑	↑
Salt	↓	↓	

CURRENT AND POTENTIAL APPLICATIONS

- *Lightweight structures*
- *Separations*
- *Chromatographic Substrates*
- *Absorbents*
- *Barriers*
- *Insulation*

EMULSION FOAM ADVANTAGES

- **Simple and Straightforward**
- **Large and Small Sizes**
- **Variable Microstructure**
- **Variable Chemistry**
- **Can be Modified**
- **Can be Machined**
- **Can be Pumped and Molded**
- **Non-CFC, Water-Based**

MICRO/MACRO STRUCTURAL DESIGN OF CERAMIC MEMBRANES

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Microstructure across the thickness of a porous ceramic membrane exhibits various morphology: symmetric vs. asymmetric and composite and tortuous vs. nearly straightpore. Examples are taken from commercial membranes. Different methods for preparing microporous ceramic membranes of desired pore morphologies are discussed including anodic oxidation, track etching, phase separation/leaching, polymerization, pyrolysis, thin film deposition, pore surface modification, washcoating and sol-gel process. The combination of washcoating and sol-gel processing is presently the most practiced method commercially.

The morphological and materials design of ceramic membranes can be influenced by the application requirements and prevailing transport mechanisms. Factors such as volumetric flow rate, fluid medium, pressure, temperature, retention coefficient, chemical and thermal stabilities, permeate flux and others are discussed in reference to the microstructural design and preferred preparation methods.

Current commercial ceramic membranes are dominated by three macrostructural designs: tube/tube bundle, disk and multichannel-monolithic. The monolithic configuration provides high packing density and requires lower production and maintenance costs. There are, however, other possible higher packing density configurations common to organic polymeric membranes that are still missing in the inorganic membrane industry.

The design of membrane elements, modules and systems depend on many operational considerations. Concentration polarization, fouling, packing density, ease of maintenance, mechanical strength, element end seals, housing materials and module packaging are just some examples and will be discussed.

Symmetric

Asymmetric

Straight-pore

Tortuous-pore

Anodic Oxidation Process for Making Membrane

Phase-Separation/Leaching Process for Making Porous Glass Membrane

Slip Casting/Dip Coating Method

Table 3.1. Commercial Porous Inorganic Membranes

<i>Manufacturer</i>	<i>Trade Name</i>	<i>Membrane Material</i>	<i>Support Material</i>	<i>Membrane Pore Diameter</i>	<i>Geometry of Membrane Element</i>	<i>Tube or Channel Inside Diameter (mm)</i>
Alcoa /SCT U.S. Filters	Membralox®	ZrO ₂ Al ₂ O ₃	Al ₂ O ₃ Al ₂ O ₃	20–100 nm 0.2–5 μm	Monolith/ Tube	4 and 6
Norton	Ceraflo®	Al ₂ O ₃	Al ₂ O ₃	0.2–1.0 μm 6 μm (symmetric)	Monolith Tube	3
NGK		Al ₂ O ₃	Al ₂ O ₃	0.2–5 μm	Tube	7 and 22
Du Pont	PRD-86	Al ₂ O ₃ , Mullite, Cordierite	None	0.06–1 μm	Tube	0.5–2.0
Alcan/Anotec	Anopore®	Al ₂ O ₃ Al ₂ O ₃	Al ₂ O ₃ Al ₂ O ₃	20 nm 0.1 μm 0.2 μm	Plate	
Gaston County Filtration Systems	Ucarsep®	ZrO ₂	C	4 nm	Tube	6
Rhone- Poulenc/SFEC	Carbosep®	ZrO ₂ ZrO ₂	C C	~ 4 nm 0.08–0.14 μm	Tube	6
Du Pont/ CARRE		Zr(OH) ₄	SS	0.2–0.5 μm	Tube	~ 2
TDK	Dynaceram®	ZrO ₂	Al ₂ O ₃	~ 10 nm	Tube	≤ 5
Asahi Glass		Glass	None	8 nm–10 μm	Tube/Plate	3 and 10
Schott Glass		Glass	None	10 nm and 0.1 μm	Tube	5–15
Fuji Filters		Glass Glass	None None	4–90 nm 0.25–1.2 μm	Tube	
Ceram-Filtre	FITAMM	SiC	None	0.1–8 μm	Monolith	25
Fairey	Strata-Pore® Microfiltrex®	Ceramics SS	Ceramics SS	1–10 μm 0.2–1 mm	Tube/Plate Tube Plate	10
Mott		SS, Ni, Au, Ag, Pt, etc.	None	≥ 0.5 μm	Tube	3.2–19
Pall		SS, Ni, etc.	None	≥ 0.5 μm	Tube	60 and 64
Osmonics	Hytrex® Ceratrex®	Ag Ceramics	None Ceramics	0.2–5 μm 0.1 μm	Tube/Plate	
Ceramem		Ceramics oxides	Coerdierite	0.05–0.5 μm	Honeycomb monolith	1.8

Considerations for Microstructural Design of Ceramic Membranes

Predominant transport mechanism - pore size & material

Volumetric flowrate - production vs. lab (energy & capacity)

Retention coefficient - pore size distribution & shape

Chemical resistance - pH & solvent

Thermal resistance - structural & phase change

Permeate flow resistance - membrane thickness & multilayer

Pin holes/cracks - membrane thickness & quality of support layer

Catalytic membrane reactor - membrane material & pore morphology

Separation of Gaseous Mixtures

<u>Separation by</u>	<u>Mechanism</u>	<u>Pore Diameter</u> (nm)	<u>Temp.</u>	<u>Pressure</u>	<u>Example</u>
Molecular mass	Knudsen diffusion	<100		Low	H₂/N₂
Interaction with Solids	Surface diffusion	<10	Moderate	High	H₂/H₂S
	Capillary condensation	<1	Low	High	H₂/SO₂
Size	Molecular sieving	<1			H₂/CH₄

Rejection of Dextrans by an 40Å Alumina Membrane

Hydraulic Resistance of Alumina Membrane/Support Layers (19-Channel Monoliths)

Membrane pore dia. (μm)	No. of layers	Membrane resistance as % of total resistance
0.004	4	99.6
0.025	4	92.8
0.2	3	74.0
0.8	2	36.3
2	2	17.3

Assuming resistance in series.

Membrane Reactor

- **Increase yield by displacing reaction equilibrium**

- **Enhance selectivity by removing undesired intermediate(s)**
- **Simultaneously separate products from reactants**

Considerations for Macrostructural Design of Ceramic Membranes

Flux decline - crossflow, backflushing, membrane materials

Packing density - membrane element shape & system configuration

Ease of maintenance - membrane element shape & system configuration

1/200 - 1/1000

Mechanical strength - membrane element shape

Application regulations - housing material

Connection with housing/piping - thermal expansion & chemical resistance

End seals of elements - thermal expansion & thermal/chemical resistances

Figure 5.13. Effect of sequential backflushing on permeate flux (1: flux without backflush; 2: flux with a low backflush frequency; 3: flux with a high backflush frequency).

Side View of Membrane Module Consisting of Multichannel Elements

Technical Challenge

Increasing applications in liquid phase separation & gas filtration

High temperature gas separation

Integration of membrane separation and catalysis (esp. pilot & production)

Smaller pore-size membranes

Higher packing density

Brittleness

Optimization of membrane production processes

Sol-Gel Films for Energy-Related Materials

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Through sol-gel processing, the full flexibility of solution chemistry can be exploited to make films with finely controlled compositional characteristics; no less important is the possibility of exploiting colloid and polymer physics in general ways to achieve desired film properties such as porosity. The advantages, disadvantages, and applications of sol-gel films are discussed with an emphasis on those properties that are unique to sol-gel processing.

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****DRAFT****

SOL-GEL COATINGS FOR ENERGY-RELATED MATERIALS

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ABSTRACT

Through sol-gel processing, the full flexibility of solution chemistry can be exploited to make films with finely controlled compositional characteristics; no less important is the possibility to exploit colloid and polymer physics in general ways to achieve desired film properties. The advantages, disadvantages, and applications of sol-gel films are discussed with an emphasis on those properties that are unique to sol-gel processing.

I. INTRODUCTION: A LOW-COST SOLAR CELL

O'Regan and Grätzel reported [1] in late October, 1991, that they had succeeded in fabricating a photovoltaic cell based on commercially realistic technologies. One of the enabling technologies in their device is a sol-gel coating. While this cell may not be the answer to mankind's energy problems, it serves to illustrate some of the advantages of sol-gel coatings:

The cell is based on a porous TiO_2 (anatase) coating impregnated with a charge-transfer dye, a ruthenium-pyridine complex. Electrical contact is made throughout the porous film by an iodide electrolyte. Solar photons are efficiently absorbed by the film—46% of the solar flux at all wavelengths is harvested—and their energy is converted, at efficiencies exceeding 80%, to electrons injected into the conduction band of the TiO_2 semiconductor. After the collected current was sent through test loads and back into the electrolyte to regenerate the dye, overall efficiencies between 7% and 12% were found depending on illumination. The authors reported exceptional stability for their cell with respect to decomposition under constant use. Owing to the low cost of materials, they feel that practical applications are feasible.

The success of this solar cell derives from a high quantum efficiency for charge injection as well as the substantial overlap between the absorption spectrum of the dye

and the solar spectrum. However, neither of these attributes could be exploited unless a sufficient amount of dye could be illuminated while maintaining electrical contact with both a semiconductor substrate and a regenerative electrolyte. Thus, the porosity of the titania film is a decisive advantage.

The film was deposited from a colloidal suspension of 10 nm TiO_2 particles prepared by the hydrolysis of titanium tetraisopropoxide. A "paint" of these particles was spread onto a conductive glass slide and allowed to dry into a 10 μm film. After lightly sintering the film at 450 C to ensure electrical contact, a high surface area semiconducting support resulted with pores large enough to accept dye molecules; the surface area of the cell was increased 780 fold!

Aside from the porosity, other factors contribute to the economic potential the solar cell. The purity of the titania is important, and, through the purity of the liquid reagents, it is attained. The relatively low-tech method of film fabrication requires minimal investment in equipment, yet retains wide flexibility to coat large areas or complex shapes. The thermal treatment is low in energy cost by comparison to most ceramic processing. Finally, in addition to chemical control, the manufacturer has physical control of the film precursors—the colloid—and the way they are deposited, which allows optimization of the cell performance via porosity.

II. SOL-GEL FILMS: DEFINITION AND HISTORY

No universal definition of sol-gel film processing exists. Perhaps the most general qualification is any film deposited from a liquid phase. While necessary, this qualification would be perceived too general to the current sol-gel community. Sol-gel films are defined largely by processing:

A sol-gel film is a coating or free-standing film that is formed from a sol through continuous stages of increasing concentration of a solid precursor.

This definition comes closest to modern usage [2]. Precipitations, such as common gold or silver metallizations on glass, are excluded since such a film grows essentially at final density from the substrate into the liquid. On the other hand, precipitates that form in the bulk liquid and that are then concentrated on a surface by settling, electrophoresis, or evaporation form a true sol-gel film by the above definition. A schematic of the sol-gel processing field, of which films is only a part, is shown in Fig. 1.

Typically, the sol is a solution of polymeric species or a suspension of particles including, possibly, particles in the colloidal size range. The liquid carrier must be volatile or, at least, volatilizable through heat treatment. During deposition, through states of increasing solids concentration, this sol might gel, as in bulk sol-gel processing, however, the gel state is often a fleeting transient that quickly empties of liquid. Nevertheless, the structures formed during this stage, with varying amounts of porosity, influence the structure of the final film.

By the above definition, printing and painting are sol-gel film processes. Thus, sol-gel films are easily the oldest surface modifications invented by man, dating back tens of thousands of years. The first modern sol-gel films, according to the early, definitive review by H. Schroeder [3] of Schott Glaswerke, were Langmuir-Blodgett (LB) monomolecular layers, which by 1935 had been developed to the point of making antireflection coatings. LB films are formed by the slow withdrawal of a substrate through a molecular surface layer that gets lifted off the liquid surface onto the substrate; they continue to be developed as a means of depositing very thin, high molecular weight layers, and they are considered to be a research discipline in their own right, separate from mainstream sol-gel technology.

Schroeder reports that the first oxide films (SiO_2) were made in Germany shortly before World War II by spin coating silicic acid onto glass. During the War, this process was used industrially, presumably as optical coatings, but, according to Dislich and Hinz also of Schott, the first products did not appear on the market until 1953 [4]. Large scale production of automotive mirrors coated by sol-gel techniques began in 1959. Original patents on the chemical basis of sol-gel oxide films were filed simultaneously by the Schott chemists [5] and by Levene and Thomas (Owens-Illinois, Inc.) in 1969 [6]; the process itself was known through German patents to Schott and Leitz as early as 1939 [7]. The early Schott workers nicknamed sol-gels "glass from the bottle" [4].

Dislich predicts [8] that the future of sol-gel processing will be based on its strengths: high compositional and homogeneity control at low temperatures. Sayer and Sreenivas favor sol-gel processing as a way to evaluate new compounds quickly and cheaply [9]. By comparison to vacuum and chemical vapor deposition (CVD) techniques, sol-gel coating is not equipment intensive or directional. For optical applications, the ability to coat both sides of an element simultaneously is a potential advantage [3]. Indeed, for any given application, sol-gel films may offer unique advantages.

III. METHODS OF FABRICATION

Sayer and Sreenivas [9] classify all ceramic thin film fabrication into physical techniques, including vacuum evaporation, sputtering, and ablation, and chemical techniques, such as CVD and sol-gel processing. Part of the flexibility of sol-gel processing is the option to use physical mechanisms in conjunction with chemical reactions to achieve a desired result. For example, it is now common to trap colloidal particles inside a fine sol-gel matrix to render a film antireflective [10] or colored [3]. This hybridization of chemical and physical aspects accounts for much of the recent explosion of interest in sol-gel films.

The first step in sol-gel film fabrication is to meter a well defined quantity of sol uniformly over the substrate; this can be accomplished in several ways, discussed below. Second, the liquid phase is allowed to dry; often the evaporation is spontaneous and nearly instantaneous. The film density is strongly affected by capillary forces at this stage. Finally, the film can be heated to remove traces of liquid, improve adhesion, crystallize, or sinter the material. The heating step is optional since, for many applications, the dry film emerging from the second stage is robust enough. Indeed, the ability to fabricate ceramic and organic films exclusively by room temperature processing may prove to be a great advantage for bioactive films.

Sol-gel processing is simple and economical, but, as Guglielmi points out [11], it remains largely empirical in practice: sol-gel *science* is a recent invention [2]. The outlook is bright. Since 1982, well over 500 papers have been published in scholarly journals on sol-gel films.

A. Dip Coating

Nothing could be simpler than dunking a part in a sol and withdrawing it. Figure 2 shows a side view of the process. Historically the technique of choice for optical films, this quintessentially low-tech process allows great flexibility in part size and shape with a minimal equipment investment. However, the simplicity of dip coating belies the complexity of the physics and chemistry behind it.

The coating of photographic film with a gelatinous emulsion motivated early studies of the hydrodynamic entrainment of a liquid film by a withdrawing body. The first correct treatment, by Landau and Levich [12], predicted that the entrained film thickness λ (Fig. 3) scales with the withdrawal velocity u_0 as $u_0^{2/3}$ (in the absence of evaporation) assuming simple, Newtonian viscosity. Guglielmi [13] cites a number of authors who have reported behaviors ranging from $u_0^{2/3}$ down to $u_0^{0.1}$, demonstrating, perhaps, that viscosities are not always simple or that surface-tension gradients are sometimes important. In any case, the interplay of gravity, surface

tension, and fluid viscosity determines the amount of liquid metered onto the surface in dip coating in contrast to slot and roller coating, in which the liquid volume is dispensed by externally controlled pressure (see below).

Most sol-gel coating is done with a volatile liquid, such as short-chain alcohols; dip coating is no exception. Evaporation during withdrawal gives rise to an astonishing phenomenon: The entrained film rapidly approaches a steady state thickness profile for a constant withdrawal velocity. A signature of this process is the presence of a "drying line" above which little or no free liquid is observed and below which the entrained liquid film tapers smoothly to the reservoir. The recession rate of this drying line is a function of its height above the reservoir, and the entrained film will rapidly grow to a length at which the recession rate matches the withdrawal rate. Typically, withdrawal speeds are of order millimeters per second, and the drying line stabilizes at a height of a few millimeters.

The steady nature of dip coating with volatile solvents engenders optical studies of the process. Schroeder [3] reports utilizing interference fringes, Fig. 4, in the film to assess coating uniformity. Since 1988 [14], Hurd and coworkers have been developing imaging ellipsometry toward this end, in which images of the steady state film through an ellipsometer yield thickness and index maps. The latter reveals a measure of the local solids concentration, while the former relates directly to the evaporation behavior. They have shown that, at the drying line, which represents a sharp edge in the evaporation and vapor diffusion problem, the sol concentrates very rapidly owing to precipitous loss of solvent [15]. This accelerated evaporation sets an unavoidable time limit on the gelation, aggregation, polymerization, or other chemistries occurring in the film, as Fig. 3 illustrates.

Surface tensions are usually finely balanced during dip coating as evinced by the fact that, except for the gravitational meniscus region, the liquid surface radius of curvature usually exceeds 1 km [16]; this point can be appreciated by the difference in scales for the measured profile $h(x)$ in Fig. 5. Surface tension is such an overwhelmingly large force, however, that dramatic things can happen when this balance is upset. The dipping of solvent mixtures having differing volatilities can lead to surface-tension gradients when one component is depleted from the mixture by differential evaporation, shown in Fig. 6. The resulting surface-driven flows produce extraordinarily high shear rates, of order 10^4 sec^{-1} , that can be used for film structure control via, for example, shear-induced ordering [17].

The uniformity of dip coated films is surprisingly good, given the fact that the sol is self-metered. Vibrations and air currents are easily and necessarily avoided; "edge-bead thickening" appears to be unavoidable [11]; good wetting is a prerequisite; phase separation in multicomponent systems can be a problem [18].

B. Spin Coating

Owing to the burgeoning microelectronics and magnetic disk industries, spin coating of sol-gel films may now be the most important fabrication technique. A sol is dispensed onto a stationary, nominally flat substrate, which is then accelerated rapidly to spin about an axis normal to the surface. A portion of the sol gets thrown off by centrifugal force. Emslie, et al [19] showed that, remarkably, the film thickness becomes uniform regardless of its starting distribution. Meyerhofer first considered evaporation in the process [20] and predicted that the film thickness should scale with the angular velocity Ω as $\Omega^{-1/2}$, a result confirmed recently by Lawrence [21]. The effects of nonNewtonian viscosity can alter this scaling, however, as discussed in Lawrence's paper. In contrast to dip coating, in spin coating the sol distributes more rapidly than evaporation effects can change its properties [11].

Shear rates in spin coating can be large enough—exceeding 10^3 sec^{-1} —to effect structural changes in the film [22]. The refractive index of silica films deposited from polysilicate sols shows an increasing trend with Ω ; intuitively consistent with the idea of shear-induced ordering, this phenomenon remains largely unexplained.

C. Electrophoresis

Possibly the only way to produce a uniform, conformal coating on complex shapes is electrophoretic deposition [23]. The part must be conductive, and the sol must contain charged species. The latter criterion can almost always be met by judicious use of emulsification or surfactancy. When the part is held in the sol at a moderate potential with respect to an inert counterelectrode—the signs depend on the particle charge—the electric field causes the particles to migrate and to adhere to the surface. Thus the film passes through states of increasing solids concentration. The coating can be built up to large thicknesses by comparison to dip and spin coating, but, if the particles are insulating, the coating itself will choke off the field.

A major advantage to electrophoretic coating is its self-healing nature. Pinholes get filled in preferentially owing to their high field strength. Similarly, edges and protruberances acquire greater thickness than flat areas. These attributes make electrophoresis attractive for microelectronic coatings [23].

D. Free-Standing Structures

A growing body of sol-gel literature deals with fibers and free-standing films of glass-forming oxides. The major part of the effort has centered in Japan,

beginning in the early 1980s. While not strictly a part of surface modification, this phenomenology deserves mention because of its intrinsic interest and the many aspects of structure formation it shares with deposited films. In fact, the coating of wires and fibers has a closer resemblance to this section than to the foregoing sections.

Sol-gel fibers were first reported by Sakka and Kamiya [24] in 1982. They allowed an alkoxide solution nearly to gel, then touched a glass rod to the surface and pulled up. A long, uniform fiber was created—a process called spinning—that became a dense glass fiber after heating. Diameters of a few microns to tens or even hundreds of microns are possible. The amount of material metered into the fiber by the gravitational meniscus has, to this author's knowledge, not been treated, although it appears to be a straightforward extension of the Landau-Levich treatment for films [12].

The characteristic of spinnability has remained a mystery. Sakka and Kozuka showed [25] that spinnable sols remain Newtonian at high viscosities and that they contain long, polymeric species as opposed to compact particles.

The same Japanese group pioneered free-standing film formation. Reviews by Sakka and coworkers in 1984 [26] and 1988 [27] treat the phenomenology. Commonly called "sheets", free-standing films have been produced in three basic ways: Sheets have been drawn from spinnable solutions using wire frames, they have been extruded through slots, and they have been coated onto substrates from which they could be separated. Typical films are tens of microns thick. Huling and Messing reported an interesting variation [28] in 1988 in which they spin coated camphor disks with various sol-gels then allowed the camphor to sublime. After firing, they produced very thin sheets, down to 1 μm thickness, of crystalline aluminosilicates.

E. Other Coating Methods

Traditional high speed, continuous coating is accomplished by premetering the sol onto a moving substrate using slots and rollers. The extensive literature on this subject has been reviewed by Scriven [29]. Though not normally considered to be in the sol-gel domain, these techniques promise to gain in importance as industrial applications are found. A recent research example that crosses the boundary into recognizable sol-gel processing is the study of "doctor-blading" by Casanova, et al [30]. Also called tape casting, the doctor blade forms a variable slit opening through which the substrate travels and the sol is dispensed.

Although spray coating, painting, printing, and many other techniques fit the definition of sol-gel films adopted here, they fall beyond the scope of this review.

IV. DRYING AND HEATING

As pointed out by Scherer [31], the removal of liquid from bulk sol-gels is particularly troublesome due to the tendency of gels to crack or warp under drying stresses. Thick films and multilayer films suffer essentially the same problems as bulk gels. Very thin films, such as those formed by dip-coating ($h < 0.2 \mu\text{m}$), tend to be below the critical thickness at which cracking occurs. In any event, capillary forces can dramatically influence the structure and porosity of sol-gel films.

1. Capillary Collapse

As soon as a gel no longer "fits" inside its host liquid volume, stress arises. In dip coating, for example, the rapid loss of liquid near the drying line creates menisci in the pores of the gel that set up tension in the liquid. The Young-Laplace equation shows that this pressure is inversely proportional to the radius of curvature of an adjacent meniscus [31]. Further evaporation is impeded by liquid transport through the gel to the gas-liquid interface, a regime called the "constant-rate period" by Scherer. For most materials, the reactive force to this tension, exerted by the interface on the gel, causes the network to collapse until such point that the gel can collapse no longer. Surface pores then emerge from the liquid as it recedes into the gel; this period is called the "falling-rate period".

A sobering calculation shows that, if the pores in the film are comparable in size to the precursor particles, then the menisci give rise to tens or even hundreds of atmospheres of tensile pressure. Whether actual pressures exceed 100 atmospheres is debatable, given the range of applicability of the Young-Laplace equation and the (meta)stability of the overexpanded liquid [17]. Nevertheless, Brinker has shown that the film compacts to a density that is proportional to the particle size owing to capillary collapse [22].

Tu and Drake [32] discuss the heat and mass transfer during a dry out process without consideration of capillary phenomena. They argue that during the constant- and falling-rate periods—called the diffusion-limited regime in their paper—not only is the transport of liquid to the evaporating interface important but also the transport of heat. In very thin films (not explicitly defined by the authors), of course, thermal transport is not limiting.

2. Stresses and Multiple Coats

Schroeder [3] identifies three stresses that can develop in sol-gel films. Intrinsic stresses are typically tensile and arise from the tendency of gels to shrink as they dry out. The fact that the gel is pinned to a substrate gives rise to adhesion stresses in this situation. Finally, thermal stress is important for materials that aren't well matched in thermal expansion coefficients.

Thermal stress is often the limiting factor in the extent to which multiple coats can be deposited. Of particular interest in this arena is the use of multiple layers to create interference optics that might meet with high temperatures. Schroeder [3] cites titania on soda-lime glass as a good thermal match—the difference in thermal expansion coefficients is less than 30%—in which repeated coats are viable. Silica, on the other hand, is not easily multicoated since its difference in thermal expansion coefficient exceeds 90%. Br utigam and coworkers [33] have found success with silica only by a full thermal treatment between layers.

The measurements of stress in sol-gel films is a science in its infancy. Schroeder used the deflection of a thin disk coated on one side to study titania films [3]. Cerqua and Hayden have applied modulated transmission ellipsometry [34] to assess residual stress as a function of various processing parameters. They found that even compressive stresses are possible depending on the age (extent of aggregation/polymerization) of the sol.

V. COMPLEX COMPOSITIONS

Since the possibilities for single-component sol-gel films are endless, the focus here is on a few examples of multicomponent formulations, the possibilities for which are even more numerous. Special applications, such as ferroelectric and superconducting films, are treated separately.

Colloidal inclusions have already been noted [3,10] as a means to modify optical properties. The use of metal and semimetal colloids or clusters remains a promising route, especially in view of recent activity with quantum-size effects in silicon.

Molecular mixtures can have equally profound optical and electronic effects. Cobalt oxide [3] was an early pigment, and mixtures of titania and silica were used industrially [4] to adjust refractive index. Cadmium stannate films were synthesized as an early transparent semiconductor.

The greatest effort appears to have gone into glass ceramic films. Dislich and Hinz [4] reported an eight-component formulation in their seminal patent [5]. An example of the extremely wide range of compositions possible by sol-gel processing is given by Puyan and Gonz lez-Oliver [35], who studied binary, ternary, and

quaternary oxides of silicon, titanium, aluminum, tin, indium, germanium, yttrium, and zirconium.

VI. APPLICATIONS

A. Electronic

There has been an explosion of papers in sol-gel processing of superconducting ceramics over the past few years, especially in Japan. The YBCO phase has been formulated [36], and Sakka's group has recently gotten involved [37]. Although reasonable critical currents (e.g. 13000 A/cm²) have been obtained, quality lags behind that of physical deposition. Nevertheless, the ease and simplicity of the sol-gel process lends itself well to a wide range of stoichiometries [38].

Ferroelectric films of the lead titanate family are under investigation in a number of labs using sol-gel technology. Phase purity is a recurring problem, as the lead-poor pyrochlore phase tends to form at low temperatures. Uhlmann and coworkers have compared these sol-gel developments, including barium and strontium titanates, to physically deposited films [39]. In general, finer stoichiometric control was possible with sol-gel as compared to sputtering, but microstructural characterization is lacking.

B. Abrasion and Wear Resistance; Strengthening

Schroeder [3] relates a curious fact: The wear and abrasion resistance of a part can be enhanced by a sol-gel coating but only if the coating is very thin (few nanometers). A similar observation was made recently by Maddalena, et al. [40], who found that the strength of soda-lime glass rods could be enhanced by thin silica coatings. In fact, they found that, if the coating is too thick ($h > 0.2 \mu\text{m}$), the strength of the rod decreases. Apparently the well known smoothing action of conformal sol-gel coatings works to repair surface defects that might otherwise nucleate a crack or abrasion.

C. Membranes

Ceramic membranes find application in food, chemical, and pharmaceutical separations for gases, liquids, and molten metals. Recently, membranes have been developed through sol-gel processing [41]. The sol-gel advantage is the control over

porosity one has by controlling the size and ramification of precursors. The inclusion of zeolites in a dense sol-gel matrix provides a second route toward well defined pores, as reported by Bein and coworkers [42].

D. Solar

Apart from the photovoltaic cell example that opened this article [1], solar applications have been focussed on the economical preparation of solar mirrors [43]. Coatings have been used to planarize low quality surfaces for later coating with a reflective layer [44]. Similar coatings have been used as protective films on solar mirrors [45] and as antireflective films [46].

VII. CONCLUSIONS

Surface modification by sol-gel films is a growing area of research for several good reasons. Sol-gel processing provides the flexibility and stoichiometric accuracy of solution chemistry while requiring relatively little or no heating and minimal equipment. The high cost of pure liquid reagents usually is not important when making thin films, but the necessity to filter reagents in critical applications could be a drawback.

No attempt was made at comprehensive coverage in this review. Rather, the examples were chosen to be illustrative. To those authors whose work was left unmentioned, the author extends his apologies in advance.

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FIGURES

1. Sol-gel processing road map (courtesy of Jeff Brinker). Film formation is one possible branch; porous (xerogel) films have wide application even when only lightly heat treated.
2. Dip coating schematic. In general, the substrate can be inclined at an angle α in order to vary the amount of gravitational draining. Above the "stagnation point" all streamlines, and therefore all solids, are entrained. The "drying line" is defined as $x=0$.
3. Stages of film formation in dip coating. In other types of coatings, many of these same stages occur but not simultaneously.
4. Interference fringes in an entrained film of ethanol being drawn from a beaker (bottom). The height of the film is a few centimeters.
5. Thickness profile of dip coating film of pure alcohol. The parabolic shape is a consequence of evaporation effects.
6. Thickness profile of a propanol/water mixture. The more volatile alcohol is essentially completely evaporated by $x=x_2$ while the water lasts until x_1 .

SOL-GEL-PROCESSING

Fig 1 Hurd

Fia Hurd

Fig 5 χ_d

Sol-Gel Films for Energy Related Materials

- Alan J. Hurd
- Ceramics Processing Sciences Department
- Sandia National Laboratories
- Jeff Brinker—Sandia
- Randy Schunk—Sandia
- Carol Ashley—Sandia
- Rich Cairncross—University of Minnesota
- Jeff Zink—UCLA
- Bruce Dunn—UCLA
- John McKernan—UCLA
- Fund Matsuda—UCLA

Lausanne Solar Cell

O'Regan & Gratzel

Nature 353, 737 (1991)

- ruthenium-pyridine dye
- exceptional stability
- good solar spectral overlap
- low cost, high efficiency (7% - 12%)

Sol-Gel Film Technology

1959 (Schott)

- Deposition technology
- Porosity control
- Solar applications
- Optical applications
- Corrosion barriers
- Thermal barriers
- Separation membranes
- Sensors
- Abrasion resistance
- Microelectronic films

Coating with Sol-Gel Films

- Dip coating
- Meniscus coating
- Spin coating

"A sol-gel film is a coating formed from a sol through continuous stages of increasing concentration of a solid precursor."

Technological

II

Sol-Gel Processing

Technological Relevance: Dense ceramic films for protection, reflectance ..., porous films for membranes and sensors ... Fibers for refractory textiles...

NONCONSTANT EVAPORATION MODEL

solve ventilation problem near tip

EVAPORATION-INDUCED CROWDING

Half the distance between particle neighbors is covered in the last 2% of the

with pyradine

MODELLING OF FILM DEPOSITION

EFFECT OF POROUS SUPPORT?

- dry: slip-casting
- filled with ROH/H₂O
- reservoir for reagents

FIBER DRAWING OF ALUMINA-BASED SOLS

MOIST AIR LEADS TO CONDENSATION ON FIBER

Porosity Control

- reactivity
- interactions
- precursor size
- fractal dimension
- heat treatment
- capillary pressure

$$p = - \sigma \cos(\theta) / R$$

$\sigma \approx 10 \text{ atm}$

Solar Mirror Planarization

Ashley & Reed, MRS Symp

121, 635 (1988)

low cost,
rough surface

- surface tension effect
- low-cost alternative
- improves corrosion, abrasion resistance
- "spin-on-glass" for microelectronics

sol-gel
planarizing
layer

high
reflectivity
surface

Meniscus Coating for Large Optics

J. A. Braken & J. M. Thomas
RCC V MRS Symp Proc 27, 413 (1992)

- requires small suspension volumes
- amenable to multilayer coatings
- minimum cross contamination between baths
- 1% reflectivity deviation over 30 cm

MICROSTRUCTURAL DESIGN OF FOAMS

**James H. Aubert
Department 1815
Sandia National Laboratories
Albuquerque, NM 87185**

Polymer properties can often be enhanced by the incorporation of porous structure due to the effect of porosity on mechanical properties, electrical properties, permeability, and adsorption and release characteristics. By manipulation of porosity on length scales from Angstroms to microns, one can vary the density, surface area, and surface activity of a polymer, and thereby vary these properties over a considerable range. For example, one can vary the micron scale porosity (and determine the transport properties) and the Angstrom length scale (and determine the adsorption characteristics) of carbon foams prepared via pyrolysis of polyacrylonitrile foams used for gas adsorption. The systematic exploitation of these multi-length scale porosities, however, has lagged due to the complexity and lack of understanding of systems processed far from equilibrium. This article will describe advances in the control of physical processes which control length scales in phase separating polymer systems. The resulting porous polymers have found applications in diverse areas including: structural foams, lowdielectric films, battery electrodes, gas storage media, and biomedical devices.

MICROSTRUCTURAL DESIGN OF FOAMS

J. H. AUBERT, 1815, SANDIA NATIONAL LABORATORIES

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INTRODUCTION

TIPS PROCESS

**MORPHOLOGICAL
CONTROL**

APPLICATIONS

CONVENTIONAL FOAMS

- LARGE CELLED (e.g. 100 micromet
- LIMITED DENSITY
- OFTEN CLOSED CELLED and hard
- NOT VERSITILE for a research prog

THERMALLY-INDUCED PHASE SEPARATION (TIPS)

FOAM MORPHOLOGY IS DETERMINED FROM
PHASE SEPARATION THERMODYNAMICS

NUCLEATION AND GROWTH

NUCLEATION AND GROWTH

EARLY STAGE SPINODAL STRUCTURE

QUENCH RATE DEPENDENCE

TA0022.05.01

Fig. 1. Results for coarsening studies on demixed polystyrene/cyclohexane solutions from ref. [3]. Polystyrene $M_w = 2.23 \times 10^6$, quench temperature 27 C.

COARSENING MECHANISMS

FLOW PROCESS

$$d \sim t$$

DIFFUSION PROCESS

$$d \sim t^{1/4} \quad \text{TRANSIENT}$$

$$d \sim t^{1/3} \quad \text{ASYMPTOTIC}$$

MODEL FOR POLYMER SOLUTIONS

$$(d^\beta) = \frac{[32 D_{ps}^\beta c_s^\beta c_p^\beta \sigma (v_p - v_s)]^{1/3} [2(c_p^\alpha / c_p) - 1]^{2/3}}{[9 kT c_p^\alpha]^{1/3}} t^{1/3}$$

COSOLVENTS

DIOXANE : ISOPROPANOL

ISOTACTIC POLYSTYRENE

TIPS PROCESSES

PROCESS VARIABLES

CONCENTRATION
QUENCH RATE
SOLVENTS/COSOLVENTS

MOLECULAR WEIGHT
QUENCH TEMPERATURE
CRYSTALLINITY

MORPHOLOGICAL CONTROL

ADVANCED RECHARGEABLE BATTERIES

Ni-Cad Battery Disadvantages

1. Cd to be phased out by EPA regulations
2. Energy density 3X lower than Li battery

Li Battery Disadvantage: limited # recharge cycles due to shorting by Li dendrites

Japanese Idea: anode is carbon intercalated with lithium - eliminates dendrites

R. R. Lagasse and F. M. Delnick SNL,A

APPLICATIONS

HIGH ENERGY PHYSICS

FILTRATION

BATTERY ELECTRODES

CATALYST SUPPORTS

NATURAL GAS STORAGE

LOW-DIELECTRIC FILMS

BIOMEDICAL

CHALLENGE: EFFICIENT, INEXPENSIVE STORAGE OF NATURAL GAS

Option 1: Pressurization to 3000 psi

Gas volume = 160 times storage volume

Option 2: Adsorption on Porous Carbon @ 500 psi

Gas volume = 100 times storage volume

Goal: Gas Volume = 175 Times Storage Volume
at 500 psi.

R. R. Lagasse SNL,A

CARBONIZED PAN FOAMS

- FOAM STRUCTURE MAINTAINED WITH CARBONIZATION
- PROPERTIES DEPENDENT ON CARBONIZATION TEMPERATURE
- UNIFORM INCORPORATION OF ADDITIVES
 - CATALYTIC METALS BY ORGANOMETALLIC DECOMPOSITION
- ELECTRICALLY CONDUCTIVE COMPOSITES
- POROUS ELECTRODES

POROUS POLYMER FILMS WITH LOWERED DIELECTRIC CONSTANTS

- Dielectric Layers for Multi-chip Modules to improve computing speed.
- Dielectric constant is lowered by making the polymer porous.
- Discussions with IBM are currently underway.

BIOMEDICAL APPLICATIONS

- * VASCULAR GRAFTS**
- * ARTIFICIAL SKIN**
- * ARTIFICIAL ORGANS**
- * NERVE REGENERATION PATHWAYS**
- * CONTROLLED DRUG DELIVERY**

0052

20KV

5um

VERSITILITY OF TIPS

- * APPLICABLE TO ANY SOLUBLE POLYMER**
- * MORPHOLOGY CONTROLLED BY PHASE SEPARATION PROCESS - GREAT MORPHOLOGICAL VARIATION POSSIBLE**
- * DOPING AVAILABLE WITH TWO SCHEMES**
- * THICK STRUCTURES CAN BE PREPARED**
- * DENSITY RANGE**
- * OPEN-CELLED MORPHOLOGY INHERENT**

NANOSTRUCTURE ENGINEERING OF COMPLEX MATERIALS

DALE W. SCHAEFER

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1. Structure, Fractals and Scattering

2. Chemical Factors: Solution Polymerization

K. Keefer, C. Ashley, J. Brinker

3. Physical Factors: Phase Separation

R. Pekala, L. Hrubesh, G. Beaucage

Application Small-Angle Scattering to Porous Ceramics

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1. Structure, Fractals and Scattering

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6/15/93-Scott/Fractals.PPT-5

Scattering from Porous Materials

6/15/93-Scott/Fractals.PPT-6

Structure Development During Sintering

POLYMERIC
COLLOIDAL

©1993-SocSciFractal PPT-7

Polymeric Solids from Silicate Precursors

Mat. Res. Soc. Symp. Proc. 73, 277 (1987)

STRUCTURE DEPENDS ON
PRECURSOR CHEMISTRY

AGING

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Coupling of Chemical and Physical Processes

Chemical Process

Physical Process

6/15/93-Scott/Fractals.PPT-9

Chemistry Determines Branching

POLYMERIZATION OF SOLUBLE SILICATES

NETWORK

J. de Phys. (Colloq.) C4, 121 (1989).

6/15/93-Scott/Fractals.PPT-10

Scattering From Fractals

$$I_{\text{POROD}}(Q) \sim M^2 (QR)^{-X} = S$$

$$M \sim R^D$$

$$S \sim R^{D_s}$$

D = Mass Fractal Dimension

D_s = Surface Fractal Dimension

$$I(Q) \sim R^{2D} (QR)^{-X} \sim R^{D_s} \quad X = 2D - D_s$$

0/15/93-ScattFractals.PPT-13

Interpretation of Power-Law Profiles

$$I(Q) = Q^{-2D+D_s}$$

POROD SLOPE

SMOOTH SURFACE

-4

ROUGH SURFACE

-3 TO -4

NETWORK POLYMER

-1 TO -3

GRADED INTERFACE

<-4

0/15/93-ScattFractals.PPT-14

Structure of Silica Aerogels

Polymeric
2-Stage
Acid-Base

Rough Pores
2-Stage
1000° C Sinter

Microphase
1-Stage
Base

6/15/03-Sci&Fractals.PPT-15

Nucleophilic Substitution Favors Monomer-Cluster Growth

671503 Silses Polymer-3

Slow Hydrolysis Favors Monomer-Cluster Growth

Why Does Roughness Depend on H_2O

671503 Silses Polymer-4

Coupling of Chemical and Physical Processes

Chemical Process

Physical Process

6/15/93-Phase Separation-1

Porosity Control: RF Aerogels

R. W. Pekala, LLNL

6/15/93-Phase Separation-2

Catalyst and Density Dependence

Catalyst

Density

$$\lim_{(Qd_x \gg 1)} \frac{d\Sigma(Q)}{Vd\Omega} = 2\pi(\Delta\rho)^2 S_v Q^{-4} \equiv KQ^{-4}, \quad Qd_x \gg 1$$

$$S_v = 180 \text{ m}^2/\text{cm}^3$$

6/15/93-Phase Separation-3

Porod Analysis

$$\lim_{(Qd_x \gg 1)} \frac{d\Sigma(Q)}{Vd\Omega} = 2\pi(\Delta\rho)^2 S_v Q^{-4} \equiv KQ^{-4}, \quad Qd_x \gg 1$$

$$d = \frac{4}{S_v} = \phi_s d_s + \phi_p d_p$$

$$\phi_s = \frac{\rho}{\rho_s}$$

6/15/93-Phase Separation-4

Solid Chord Independent of Density

6/15/93-Phase Separation-5

Length Scale Determined by Crosslinking

6/15/93-Phase Separation-6

Elasticity

$$R \sim M^{1/2}$$

DOMAIN GROWTH CONTROLLED BY
THERMODYNAMICS NOT KINETICS

©15/03-Phase Separation-7

Silicone Microcomposites

©15/03-Phase Separation-8

Dependence on Elastic Chain Length

Competing Interactions (Elasticity vs Incompatibility) Lead to Microphase Separation.

6/15/03-Phase Separation-6

**POROUS MATERIALS
CHARACTERIZATION
AND RESEARCH ON
POROUS MATERIALS
IN FOREIGN COUNTRIES**

**Douglas Smith
UNM/NSF Center for Micro-Engineered Ceramics
University of New Mexico**

UNM/CMEC

CURRENT CHARACTERIZATION TECHNIQUES

- 1) GAS ADSORPTION**
- 2) MERCURY POROSIMETRY**
- 3) OPTICAL MEANS**
- 4) SCATTERING**
- 5) PERMEATION/DIFFUSION**
- 6) NMR**

ADSORPTION/CONDENSATION

TOTAL PORE VOLUME
if all pores < ~100 nm

PORE SIZE DIST.

Kelvin Equation

$1 \text{ nm} < r < 100 \text{ nm}$

percolation effects

SURFACE AREA INFORMATION

BET Theory

Problems if:

1) Microporous

2) Macroporous

ADSORPTION - MICROPOROUS SOLIDS

? How to relate adsorption to pore size.

MERCURY POROSIMETRY

Basic principle: Force a non-wetting fluid into pores.

PROBLEMS: Sample compression, percolation effects,
pore size range ($3\text{nm} < r < 10\text{ }\mu\text{m}$), destructive,
 θ and γ uncertainty

SCATTERING

ADVANTAGES:

**RELATIVELY FAST, LARGE RANGE OF LENGTH
SCALES, PROBES CLOSED POROSITY,
WET SAMPLES POSSIBLE**

DISADVANTAGES:

**RELATING SCATTERING INFORMATION TO PORE
STRUCTURE, PROBES CLOSED POROSITY,
EXPENSIVE, MULTIPLE INSTRUMENTS
NECESSARY FOR WIDE SIZE RANGE**

SMALL ANGLE X-RAY SCATTERING

Guinier Region

Provide information on mass distribution in porous materials

R_g = radius of gyration

Porod Region

Information on fractal structures

$$P = -X = -2d_f + d_s$$

SAXS WITH CONTRAST MATCHED ADSORBATES

WHY?

Density determination, pore vs particle.

"Real" pore size distribution.

Micropores.

Pore shape.

1.a Pore Morphology

1.b Surface Roughness

1.c Pore Size

UNM/CMEC

SAXS WITH CONTRAST MATCHING

NOTE: $I_0 = I_c (\rho_1 - \rho_2)^2$

PORE STRUCTURE ANALYSIS VIA NMR

- 1. LOW FIELD NMR OF WET MATERIALS**
- 2. MAGNETIC RESONANCE IMAGING [MRI]
(SPATIAL RESOLUTION)**
- 3. ^{129}Xe NMR FOR MICROPOROUS MATERIALS**
- 4. PULSED FIELD GRADIENT NMR
MEASUREMENTS OF DIFFUSIVITY**

DIFFUSION/PERMEATION MEASUREMENTS

USUALLY APPLICATION SPECIFIC

MEMBRANES - PERMEATION AND SELECTIVITY

PROBLEMS: slow, knowing the thickness of the separation layer, multiple transport regimes possible, pore size distributions.

ADSORBENTS/CATALYSTS/IX
- TRANSIENT UPTAKE
PROBLEMS: Particle size dist.,
Pore size distribution, relating
Diffusivity to pore size

PORE STRUCTURE CHARACTERIZATION AT UNM

- **6 adsorption analyzers including ASAP 2000(2) and VTI 500 psi combined adsorption/Varian 400 MHz NMR apparatus, gas permeation, wet gel permeability, mercury porosimeter, Surface Acoustic Wave (SAW) adsorption analyzer for thin films, combined adsorption/dilatometer.**
- **Scattering Including, 12 KW rotating anode generators(2), Kratky, Pinhole and Bonse-Hart optics for SAXS, X-ray reflection for film analysis, INEL CPS-120 for high T XRD, 3 light scattering setups for static and dynamic scattering.**
- **Low field NMRs: 10 MHz, 20 MHz, 4-60 MHz, for "wet" materials.**
- **Hitachi S-800 SEM (2nm resolution) with x-ray and image analysis.**
 - **Membrane characterization; single gas permeability (2), multi-component gas separation**

RTA IN POROUS MATERIALS

RESEARCH NEEDS

- 1) NEW EXPERIMENTAL TECHNIQUES
(PROBABLY BY COMBINING CURRENT TECHNIQUES)**
- 2) BETTER THEORIES TO RELATE ADSORPTION
ISOTHERMS TO PORE STRUCTURE.**
- 3) MODEL POROUS SOLIDS WITH DIAMETERS
BETWEEN 1 AND 2 nm.**
- 4) FASTER ANALYSIS TIMES**
- 5) ON-LINE MEASUREMENT**

**POROUS MATERIALS
RESEARCH OVERSEAS**

**POROUS MATERIAL CHARACTERIZATION:
UK AND FRANCE, ACKNOWLEDGED LEADERS**

**INORGANIC MEMBRANES:
NETHERLANDS, FRANCE, JAPAN**

MAJOR GOVERNMENT DIRECTED EFFORT IN JAPAN

**CENTRAL GOVERNMENT SUPPORT FOR POROUS
MATERIALS IN BOTH JAPAN AND EC.
NO NSF/DOE/ETC. PROGRAM SPECIFICALLY
IN POROUS MATERIALS**

POROUS MATERIALS FORUM JAPAN- FALL 1992

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Figure 1 Distribution of authors by country.

B

Figure 2 Papers by application area
(for application specific papers).

UNIMOD

CHARACTERIZATION OF POROUS SOLIDS-COPS

COPS III, 1993 183 Papers

COPS II, 1990 82 Papers

UNM/CMEC

**Poster Session Abstracts
(Titles and Authors)**

**DOE POROUS EXPO
POSTER SESSION ABSTRACTS**

“Preparation and Properties of Porous Ceramics using SiO₂ Coated Powders,” by Dr. Lynn Neergaard, Mohamed B. Nawaz, and Yidong Tong, Materials and Metallurgical Dept., New Mexico Tech, Socorro, NM 87801.

“Insoluble Chemical Tags: A New Application of Zeolite Molecular Sieves,” by Mark Phillips, Dept. 1846, Sandia National Labs, Albuquerque, NM 87185.

“Semi-Crystalline Microporous Structure Formation,” by A. Laxminarayan, K. S. McGuire, and D. R. Lloyd, Dept. of Chemical Engineering, University of Texas @ Austin, Austin, Tx 78712.

“Computer Aided Molecular Analysis of Imogolite,” by P. I. Pohl and D. M. Smith, Department 6622, Sandia National Laboratories, Albuquerque, New Mexico 87185.

“Preparation of Mixed-Metal Oxide Particles having High Reactivity, Macroporosity and Attrition-Resistance,” by R. Gupta, S. K. Gangwal, and S. C. Jain, Research Triangle Institute, Research Triangle Park, NC 27709.

“Unique Properties of Nanoporous Aerogels for Thermal, Acoustic, and Dielectric Applications,” by L. W. Hrubesh and R. W. Pekala, Lawrence Livermore National Laboratory, P.O. Box 808, Livermore, CA 94550.

“A New Look at Carbon Black,” by J. Wilson and U. Boes, Cabot Corporation, 157 Concord Road, Billerica, MA 01821

“Nanochannel Dielectric-Conductor Composites for Photonics and Microelectronics,” by C. A. Huber, T. E. Huber, and J. A. Lubin, Naval Surface Warfare Center, Code R36, 10901 New Hampshire Ave., Silver Spring, MD 20903-5000.

“Porous Metal Oxide Supports, Preparation, Properties, and Commercial Applications,” by T. Szymanski, Norton Chemical Process Products Corp., P.O. Box 350, Akron, OH 44309-350.

“New Synthetic Approaches to Microporous Layered Materials,” by K. A. Carrado, Chemistry Division, Argonne National Laboratory, Argonne, IL 60439.

“Fluid Flow Through Low Density Materials With Mesoscopic Disorder,” by D. F. Calef, E. A. Chandler, and A. J. Ladd, Lawrence Livermore National Laboratory, Livermore, CA 94550.

“NMR Measurement of Pore Sizes,” by Y-W. Kim, D. M. Smith, and W. L. Earl, UNM/NSF Center for Microengineered Ceramics and Chemistry and Laser Sciences Division, Los Alamos National Laboratory, MS G740, P.O. Box 1663, Los Alamos, NM 87545.

“NMR Measurement of Pore Sizes,” by Y-W. Kim, D. M. Smith, and W. L. Earl, UNM/NSF Center for Microengineered Ceramics and Chemistry and Laser Sciences Division, Los Alamos National Laboratory, MS G740, P.O. Box 1663, Los Alamos, NM 87545.

"Design and Synthesis of Selective Sorbents," by W. L. Earl, Chemistry and Laser Sciences Division, Los Alamos National Laboratory, MS G740, P.O. Box 1663, Los Alamos, NM 87545.

"Synthesis of Porous B-N," by R. T. Paine, J. J. Janik, M. M. Fan, W. C. Ackerman, D. W. Hua, W. C. Fahrenholtz, and D. M. Smith, Departments of Chemistry and Chemical Engineering, University of New Mexico, Albuquerque, NM 87131.

"NMRI of Multiphase Flows," by A. Caprihan and M. Nakagawa, Lovelace Medical Foundation, 2425 Ridgcrest Dr. S.E., Albuquerque, NM 87108-5127.

"Pore Structure Analysis via Small Angle X-ray Scattering and Contrast Matching," by D. W. Hua, J. V. D'Souza, P. W. Schmidt, and D. M. Smith, UNM/NSF Center for Micro-Engineered Ceramics, University of New Mexico, Albuquerque, NM 87131.

"The Use of Imogolite as a Pore Size Standard in the Size Range of 0.8 to 1.2 nm," by W. C. Ackerman, D. W. Hua, Y. W. Kim, J. C. Huling, and D. M. Smith, UNM/NSF Center for Micro-Engineered Ceramics, University of New Mexico, Albuquerque, NM 87131.

"Preparation of Low-Density Aerogels at Ambient Pressure," by J. M. Anderson, R. Deshpande, J. L. Thole, X. Qiu, D.-W. Hua, and D. M. Smith, UNM/NSF Center for Micro-Engineered Ceramics, University of New Mexico, Albuquerque, NM 87131.

"Scattering Characterizations of Microporous Gels and Foams," by G. Beaucage, Dept. 1815, Sandia National Laboratories, Albuquerque, NM 87185.

"Environmentally-Sound Removable Foam Encapsulants," by C. Arnold, Jr., P. B. Rand, D. K. Derzon, and J. S. Kawola, Dept. 1811, Sandia National Laboratories, Albuquerque, NM 87185.

"Sandia National Laboratories Battery Technology Initiative (BTI)," by S. I. C. Levy, Dept. 2523, Sandia National Laboratories, Albuquerque, NM 87185.

"Tailored Microcellular Polymers and Carbon at Sandia National Laboratories / New Mexico & California," by William R. Even and Robert R. Lagasse, Sandia National Laboratories, Livermore, CA and Albuquerque, NM.

"Bridged Polygermsesquioxanes. Organically Modified Germanium Oxide Materials.," by G. M. Jamison, D. A. Loy, and K. J. Shea, Dept. 1811, Sandia National Laboratories, P.O. Box 5800, Albuquerque, NM 87185.

"Bridged Polygermsesquioxanes. A Novel Class of Porous Siloxane Materials.," by D. A. Loy and K. J. Shea, Dept. 1811, Sandia National Laboratories, P.O. Box 5800, Albuquerque, NM 87185.

"Porous Materials for Catalytic and Radioactive Waste Applications," by E. Klavetter, R. Kottenstette, S. Lott, and L. McLaughlin, Dept. 6212, Sandia National Laboratories, P.O. Box 5800, Albuquerque, NM 87185.

“Gas Separation by Fullerene Membranes,” by R. A. Assink, J. E. Schirber, D. Loy, and B. Morosin, Dept. 1812, Sandia National Laboratories, P.O. Box 5800, Albuquerque, NM 87185.

“Zirconium Silicate Polymer-Derived Membranes for Gas Separation,” by J. Mendez-Vivar, D. M. Smith, D.-W. Hua, R. A. Assink, and C. J. Brinker, UNM/SNL Advanced Materials Laboratory, 1001 University Blvd. SE, Albuquerque, NM 87106.

“Highly Porous Graphitic Microtubule Structures,” by Robert W. Hausslein, Hyperion Catalysis International, Inc., 38 Smith Place, Cambridge, MA 02138.

“Microcellular Polymer and Carbon Foam Produced at the U.S. Department of Energy, Oak Ridge Y-12 Plant, Using a Thermally Induced Phase Inversion Process,” by R. F. Simandl, J. D. Brown, and T. L. Clift, Martin Marietta Energy Systems, Inc., Y-12 Plant, Bldg. 9202, Oak Ridge, Tenn 37831-8095.

“Porous Thin Films of Hydrous Metal Oxide Ion-Exchange Materials,” by C. S. Ashley, A. G. Sault, T. J. Gardner, S. Srinivasan and A. K. Datye, Dept. 6211, Sandia National Laboratories, Albuquerque, NM 87185.

“Fabrication and Application of Dense Inorganic Membranes,” by A. Deshpande, J. E. Ellison, C. Xia, and T. L. Ward, Dept. of Chemical and Nuclear Engineering, University of New Mexico, Albuquerque, NM 87131.

“Sol-Gel Routes to Porous Metal Oxide,” by C. Roger and M. J. Hampden-Smith, Dept. of Chemistry and Center for Micro-Engineered Ceramics, University of New Mexico, Albuquerque, NM 87131.

“Molecular Recognition on Macroporous Polymers,” by K. J. Shea, Dept. of Chemistry, University of California Irvine, Irvine, CA.

“Drying of Ceramic Compacts,” by M. W. Weiser, K. B. Fong, D. M. Smith, and S. Thoma, Center for Micro-Engineered Ceramics, University of New Mexico, Albuquerque, NM 87131.

“Microcellular Carbonized Foams as Catalysts and Catalyst Supports,” by C. Quintana, A. Sylwester, L. Whinnery, W. Even, and A. Sault, Dept. 6211, Sandia National Laboratories, P.O. Box 5800, Albuquerque, NM 87185.

“GASAR Materials: Production of Porous Metals through Gas-Eutectic Solidification,” by D. M. Walukas and V. I. Shapovalov, DMK Tek, Inc., 717 E. Huron St., Ann Arbor, MI 48104.

Workshop Summaries

Workshop Summaries

On the following several pages, you will find summaries of the EXPO Workshops, as provided by their respective Chairs. We hope you will find it useful to have available this synopsis of workshop discussions. Our goal was to stimulate discussion, and to provide feedback to the DOE on issues such as industrial needs, the most appropriate role of the DOE and the National Labs in future interactions, and best routes to commercialization. Based on the workshop summaries, we feel that goal was completely met.

Although the individual workshops covered a wide range of technical areas, a few common threads may be found running through the discussions. For example, most of the workshops mentioned a need for the National Labs to be a resource for basic work that is no longer supported sufficiently by industry due to financial pressures. Additionally, many of the workshops emphasized the need for better communication and/or collaboration among the interested parties. Sponsorship of meetings such as this EXPO, the formation of consortia, and the formation of national technical centers were all discussed.

The EXPO organizers wish to thank each of you who participated in the workshops for stimulating discussion and providing useful suggestions to our DOE sponsor.

- Cliff Renschler -

GAS SEPARATION

Moderators: D. E. Fain and P.D. Ries

INDUSTRIAL NEEDS:

Industrial relevant gas separations identified were; O₂/N₂, H₂/CH₄, H₂/CO & CO₂, H₂/Hydrocarbon (liquid and gaseous), H₂/H₂S, CH₄/N₂, CH₄/CO₂, air/VOC, air/H₂O, air/acid gases (NO_x & SO_x), and He/hydrocarbons. Among the participants, O₂/N₂/ ranked first while H₂/CH₄ and H₂/CO & CO₂ separations in second place.

The three technologies to accomplish these separations are cryogenic fractionation, pressure swing adsorption (PSA), and membranes. We concentrated on PSA and membrane technology as these require porous materials. Although these appear to be competing technologies there are applications that favor one over the other. Factors to be considered are product purity, productivity, cost, and space requirements.

Research needs were identified for organic and inorganic membranes as well as improved PSA absorbents. For membranes increased selectivity permeability, and fabrication methods were mentioned. Better N₂ absorbents with higher capacity are needed to produce O₂ using PSA.

MECHANISM FOR INTERACTIONS:

In our group several ideas about industry/government laboratory/university interactions could be accomplished through a variety of mechanisms. Consortia could be used for pre-competitive projects while CRADAs would allow individual projects to proceed. The pre-competitive areas are those fundamental research and development needs of an industry that they do not have the resources to carry out but require to remain competitive. Industry input should be solicited in order to focus these research efforts but retain enough flexibility to allow for innovation. The economics and manufacturability are key issues that need to be addressed in the early stages to increase the chances of commercialization.

DOE'S ROLE:

DOE and industry should work together at identifying strategic technology needs and provide the mechanisms by which the research can be accomplished in a timely manner. There was also concern over how the national laboratories determine their overhead charges. The differences between government and private sector accounting systems make it difficult to determine the value of in kind research.

CATALYSTS AND FUEL CELLS

Moderators: Alan Sylwester, Len Marianowski, and Gary Carlson

Industry requires catalysts for cleaner, safer and more competitive processes. As a result, catalysts have a pervasive impact in our economy. Catalytic processes account for approximately 20% of the US GNP (\$1 Trillion) and associated jobs as well as a \$180 Billion export market which contributes to a positive trade balance for the US. The \$2.1 Billion catalyst market in the US supports petroleum refining (35%), chemical processing (31%) and environmental applications (34%). Improved catalysts and porous material are necessary to meet significant challenges such as those imposed by the 1990 Clean Air Act which requires improved catalytic converters for automobiles. Improves catalysts and catalytic processes will help t enhance the US competitiveness while improving the environment.

Many industry needs in catalysis relate to an increasing emphasis on natural gas utilization (e.g., reforming, direct oxidation) driven by the increasing national emphasis on the use of natural gas as an alternative chemical feedstock and as a feedstock for alternative fuels (especially methanol). Identified industry needs in catalysts include:

Porous Carbon Materials

- * Improved catalyst stability (e.g., chemical, physical)
- * Modeling of pores and molecules in micropores
- * Reduced solid waste (gasify or regenerate spent carbon catalyst/support)
- * Improved catalytic metal dispersion

Tailored Thin Films

- * Deposition of thin film catalysion inexpensive supports
- * Control of properties including: pore structure, volume fraction, thickness, physical properties (e.g., abrasion, attrition resistance).

Shape and Size Selective Catalysts

- * Reduced severity conditions and reduced waste
- * Methane to methanol (partial oxidation)
- * Computer modeling

Membrane-Supported Catalysts

- * Controlled pore sizes
- * Robust thin films (e.g., high pressure drop, high temperatures)
- * Generic application to common supports (reduced cost)
- * Dehydrogenation of alkanes to produce olefins (energy savings)
- * Support modification to suppress mobility of dispersed catalysts.

General Issues in Catalysis/Porous Materials

- * Improved catalyst (active metal) dispersion
- * Hydrophilic/hydrophobic surfaces
- * Acidity control
- * Improved deactivation (e.g. coking)
- * Understanding of structure/activity relationships

- * Catalyst disposal (recovery/recycling of valuable materials)
- * Pollutant/environmentally-oriented applications

Fuel cells are currently used in applications including space travel, stationary power generation and transportation. Fuel cells offer promise due to their high fuel efficiency, fuel flexibility and environmental friendliness. The National Energy Strategy (NES) calls for expanded use of fuel cells and directs the Department of Energy to accelerate research and development of fuel cells to produce cost-effective alternatives over the long term. The NES reinforces Fuel Cell Systems R&D through enhanced government support, encouragement of cost-shared efforts by industry, universities and government and through the promotion of consortia and cooperative R&D.

A recent DOE initiative in fuel cells for transportation has the goal of "transparent replacement of the internal combustion engine" in transportation vehicles. In the near term, Phosphoric Acid (PA) fuel cells are receiving attention for use in buses and in the mid-term there is a push for Proton Exchange Membrane (PEM) fuel cells for light duty trucks. Long term goals would address the use of Solid Oxide fuel (SOFC) technology in similar applications. Many technical challenges must be addressed to meet these goals. Identified industry need for fuel cells include:

Porous Carbon Electrodes for PA and PEM

- * Improved porous carbons (reduced fabrication cost, chemical and physical stability)
- * Improved catalyst dispersion (reduced precious metal e.g., Pt)

Electrocatalysts

- * Non-precious metal catalysts
- * Direct methanol oxidation catalysts
- * Reforming catalysts

Porous Ceramic Electrodes for SOFC

- * Cost-effective processing/fabrication of monolithic ceramic cells and stacks (stabilized zirconia)

Membranes for PEM

- * Tailored porosity
- * High ionic conductivity
- * Chemical stability
- * Reduced cost

DOE/National Lab Roles

DOE addresses the broad National Strategic Missions of National Security, Energy Security, Environmental Compliance, Economic Competitiveness, Technology Transfer and Technology Utilization. DOE should continue to support fundamental and enabling catalyst and porous material research and development within the universities and national labs. These core programs provide many capabilities no longer available in industrial labs. National lab materials and catalyst design, porous materials characterization, tailored porous thin films, and computer modeling of porous materials are especially valued by industry.

Industry Role:

Industry should provide the applications-drives focus for collaborative work with DOE. Industry can help to provide specific objectives derived from DOE and national goals and milestones. Industry in many cases has technologies which can help DOE to achieve its missions (Spin-On). Industry looks to the national labs as sources for capabilities and technologies which industry can use to enhance national competitiveness and economic security (Spin-Off).

Mechanisms:

DOE should support industry-led pre competitive consortia and pre competitive technology partnerships between industry and labs as well as industry driven cooperative R&D (e.g., CRADAs) with the national labs. Government/Industry/National Lab/University partnerships are essential for meeting our current and future technological challenges.

ION EXCHANGE WORKSHOP

Moderators: Howard Stephens and Robert Albright

The ion Exchange Workshop was headed by Howard Stephens from Sandia National Labs and Bob Albright from the Rohm and Haas Company. There were only two other attendees in addition to the leaders. The two attendees were Mark Phillips from Sandia National Labs and Harold Huff from the Dow Chemical Company.

Some of the present needs in the ion exchange arena that were identified are listed below along with a comment as to why the present need exists.

1. Non-sluffing ion exchange polymers for the ultrapure water arena which are primarily the nuclear power generation systems and the manufacture of microchips for the computer industry. Sluffing from the presently used ion exchange polymers increases the rate of corrosion on the steam turbine blades and a higher level of defects in the making of microchips.
2. Pore systems within ion exchange polymers optimized for maximum rates of mass transport of ions and of sorbates and also optimized for capacity.
3. Improved regeneration efficiency of ion exchange polymers and polymeric adsorbents. Excess regenerant now costs twice —once for the purchase of the regenerant and second for safely disposing of it as a waste material. This second cost is relatively new as environmental impact issues continue to increase the cost for waste handling.
4. Better instrumentation for measuring liquid quality for ultrapure liquids, especially ultrapure water
5. Inorganic ion exchangers stable toward acids and bases for use in highly basic and highly acid radioactive waste clean-up.
6. Organic polymers stable toward radioactive nuclides. These materials are needed to make organic ion exchange polymers suitable for use in remediation of radioactive wastes.
7. Inorganic anion exchangers for removal of anions that hinder vitrification of radioactive wastes Inorganic anion exchangers do not presently exist, but if they did, they would simplify the removal of sulfate and bisulfate anions which hinder the vetrification of radioactive waste materials. Presently, the radioactive cesium is removed with an inorganic cation exchanger to eliminate the radioactivity from the waste so that the bisulfate and sulfate anions can be picked up by an organic anion exchanger. Following the removal of the bisulfate and the sulfate anions, the radioactive cesium loaded on the zeolite is returned to the nuclear waste for the vitrification step

8. Reagent clean-up for the electronics industry: removal of polonium from the waste phosphoric acid solutions arising from computer chip manufacturing.

FOAMS

Moderators: Bob Turner and Jim Wang

PARTICIPANTS:

Lockheed, Goodyear, Dow Chemical, Xerox, Millipore, Sandia National Laboratories, United Technology, University of New Mexico, University of Texas, and Los Alamos National Laboratories.

INDUSTRIAL NEEDS:

- Insulation: Airplane, Thermal, Electrical, and Acoustics
- Separation: Environmental, Biochemical, and Toxic
- Structure: Strong, Flexible, Permeable, Load bearing, Coating and support
- Flat sheet, thin film
- CFC elimination
- Environmental sound processing
- Convection vs diffusion in separation
- Modeling
- New foam technology
- Close cell vs open cell

DOE ROLE:

- Help implement leg. changes
- Funding - Leverage
- Cut red tape
- Intellectual rights/properties

NATIONAL LABS ROLE:

- Transfer of information
- Work on basic technology
- Work on paradigm shift
- Consultation

MECHANISM OF INTERACTION:

- CRADA
- MOU
- Secrecy
- Exchange of personnel between Labs & Industry

AREAS OF RESEARCH IMPACTING COMPETITIVENESS:

- New ways to make foams
- Modeling

Commercialization:

- High quality, low cost: Good, fast & cheap (all three)
- Technology push
- High price market
- Incentives for commercialization

Environmental Materials

Moderator: Paul Apen

Environmental material encompass a broad range of materials, applications, and technologies for waste and source reduction, energy efficiency and conservation, remediation and clean up. Many of the workshop topics, in addition to this one, concerned technologies which effectively reduce or eliminate the environmental impact of a particular material or process.

The environmental materials working group consisted primarily of industry representatives who were unfamiliar with the National Laboratories and the mechanisms currently in place for industry-lab interactions. Consequently, the focus of the discussion concerned industrial technology needs and the optimum DOE role for establishing effective public-private interactions.

Porous materials needs for environmental applications fell into three broad categories.

- (1) Waste water treatment- particle filtration and separation, corrosion inhibition, etc.
- (2) Emission controls- automotive and smokestack, SO_x and NO_x removal, etc.
- (3) Biotechnology- waste remediation, bacterial removal, etc.

Some of these are large scale environmental problems which require new porous materials, development, and processing that is effective and cost efficient. Ceramic membranes and high surface area silicas, aluminas, and zeolites are considered possible candidates.

The industrial representatives charged that DOE needs to increase communication with the private sector. In particular, the technologies, R&D activities, skills and capabilities available at the National Laboratories are not well publicized. The DOE needs to provide additional forums for private-public communication including program reviews, meetings, newsletters, and publications. This would enable the private sector to better identify available resources. The Engineered Porous Materials Expo was viewed as an excellent forum for information exchange. This format was encouraged for future meetings.

In summary, several new environmental technologies and applications are sought by industry. The National Laboratories are viewed as a source of expertise and resources. Improved communication between industry, DOE, and the Labs is required.

INSULATION

Moderator: Arlan Hunt

There were 12 participants in the workshop on insulation. Eight participants were from industry, two from national labs, and two from universities. The discussion was almost entirely concerned with silica aerogel for thermal insulation with one participant interested in aerogel for electrical insulation. There was a general consensus from the industry representatives that there was a wide spread decline in industrial basic research and that the national labs represented a valuable resource for basic studies.

The discussion concerned aerogel insulation in buildings and appliances for both industrial and residential applications. Transparent aerogel insulation for windows and skylights was discussed. Industrial need for transparent aerogel included improving and characterizing the visual clarity, determining the long term stability and the maximum size of monolithic pieces, establishing methods for quality assurance, and developing aerogel with improved elasticity. If these issues were addressed by national laboratories, then it was suggested that prototypes be produced and a formal interaction be established between a window manufacturer and a glass fabrication company.

Non-transparent aerogel insulation was discussed for markets including refrigerator and freezers, home appliances, translucent windows and skylight, electrical insulation, and high value-added niche markets. Industry needs relating to the production for aerogel included finding lower cost precursors, developing a continuous or semi-continuous production process, determining capital equipment requirements, lowering processing costs, and establishing a national aerogel processing center. Industry needs regarding the properties of non transparent aerogels including increasing R-values (currently aerogels reaches about R-12 for non-evacuated and R-32 for evacuated monoliths) by further development of infrared opacified aerogels, optimization of particle and pore size, and reduction of costs to about 10 cents/R-value per square foot. There was a short discussion regarding the electrical insulation properties of aerogel. The low dielectric constant of aerogel means that signal transmission lines and cables could transmit at close to the speed of light, a significant improvement over present dielectric. There were concerns regarding environmental issues in the production, use, and disposal of products incorporating aerogel. It was pointed out that aerogel production can recycle essentially all the solvents (primarily ethanol and carbon dioxide) and that silica aerogel at the of its life cycle is essentially sand.

Most of the industry needs outlined above could be met through National Laboratory research and development supported by DOE and transferred to industry through CRADAs.

ENGINEERED POROUS MATERIALS FOR SENSORS

Moderator: Greg Frye

At the heart of a chemical sensor is a coating material that acts as the chemical or biological interface. This material needs to take up the chemical(s) of interest with little uptake of interfering chemicals (e.g., water vapor). The chemical uptake by the coating results in a change in the physical properties (e.g., mass, conductivity, absorption of light) of the coating material. Using a transduction mechanism, these changes in physical properties are converted into changes in electrical signals that can be detected with analog to digital electronics. A variety of transduction mechanisms can be used including optical, acoustical, or electrical.

Even though the coating material is one of the smallest components of a chemical sensor system (a film with a thickness on the order of a μm and as area on the order of a cm^2), the physicochemical properties of the coating determine much of the final performance of the system. Key performance metrics that are determined by the coating material are: (1) sensitivity (determined by amount of uptake vs. concentration), (2) selectivity (determined by relative uptakes of different chemicals), (3) rapid response (determined by the time for uptake—a function of diffusion times, reaction times, etc.), (4) reversibility (determined by the strength of the binding of the chemical to the coating material), and (5) durability (the use of thin films that can easily be degraded makes this a focal point for performance degradation).

Engineered porous materials have several properties that can be used to advantage to improve chemical sensor performance. High surface area and the enhanced adsorption that occurs in micropores result in large amounts of uptake and increased sensitivity. The ability to chemically modify the surfaces can be used to provide selective adsorption or binding of the chemical species of interest. The ability for species to access the coating material through the porous network results in rapid penetration of species into the coating and rapid response. The adsorption interactions at the surfaces of the pores can be tailored to be strong enough that uptake is irreversible (useful for dosimetric type sensors) or weak enough to provide fully reversible uptake (useful for real-time, on-line monitoring application). Finally, many porous materials can be made from highly durable materials such as ceramics and glasses making them more resistant to harsh physical or chemical environments.

Regarding industrial needs, one area of interest is in environmental monitoring applications. This includes industrial monitoring of process streams for improved process control, waste streams to minimize emissions, and work-place monitors to be used during characterization and remediation of contaminated sites are needed. Another key need is automotive sensors for exhaust systems (e.g., to verify catalytic converter efficiency) and fuel injection systems (e.g., to determine fuel-air ratio). The durability of materials such as porous ceramics could be used to advantage for the application. The field of biosensors and medical test kits is another need. For this application, the porous materials are often acting as a matrix for a biologically active material or as a method for providing a small reproducible amount of biological fluid (e.g., blood) to the active sensing area. Another need identified was rapid reliable sensors for determining food quality. Finally, the use of these materials for physical sensors (e.g., temperature, pressure, light) was also discussed.

STORAGE AND ADSORBENTS

Moderators: Bill Earl and James Wegrzyn

Most of the discussion covered around mechanisms and roles in establishing interactions. There was a general feeling of frustration at making interactions work. Industry representatives would like simplified instructions on how to establish interactions and lists or facilitations for contracting in porous materials. Perhaps avoiding the bureaucracy of the laboratory Tech Transfer offices.

Issues of proprietary information and rights to intellectual property have not been resolved and are significant issues to industry. It was felt that the best role for DOE & the National Labs is in areas that affect all of the sorbents field. These are either generally applicable techniques and methods or pre competitive research.

The specific technical areas of interest are: storage of methane and hydrogen, adsorbents for pollutants and radioactive materials. These should encapsulate., adsorbents for environmental releases especially novel oil spill adsorbents. The technologies of growing interest are: Pore size measurement, standardization or cross checking of measurement techniques, structure-property relationships, natural adsorbents, systems overviews, and an understanding of tortuosity.

Industrial representatives were interested in National Lab equipment and facilities, interdisciplinary approaches, possibilities of meetings and consultations with lab personnel, and the value added by lab expertise and approaches.

BATTERIES

Moderators: George Blomgren and Jeff Braithwaite

This workshop focused on defining the porous-material needs for the industrial technologies involving electrochemical energy storage. If the performance, cost, and life of these technologies could be significantly improved, the US. consumer battery industry would be able to better compete in a world-wide marketplace and more efficient and cleaner use of electrical energy would result (e.g., through better utility transmission and distribution, substantial electric vehicle use). The development of novel porous materials, as described in this summary, probably represents a critical aspect of achieving these desired results. Consideration was given to both primary and rechargeable batteries as well as capacitors. Attendees numbered 18: 4 from industry, 5 from DOE production facilities, 7 from National Laboratories, and 2 from universities.

Although many components exist in a modern battery or capacitor, high-performance porous materials can best be used as, or part of, the electrochemically active component(s). Specifically, future activity should focus on the following four subjects: (1) carbons, (2) metal oxides, (3) conducting polymers, and (4) mathematical modeling.

The identification and improvement of porous-carbon materials is clearly the most important topic. The primary applications are as intercalation electrodes in batteries, active material/current collector in capacitors, and catalyst support in aqueous air electrodes. If these materials are to gain acceptance, the following characteristics must be improved: measurement techniques for surface properties (e.g., area, accessibility), reaction kinetics passivation (stability), and processability.

Metal oxides (e.g., RuO_2) are currently the preferred active material in capacitors. However, their cost must be dramatically reduced and more stable phase behavior achieved. Conducting polymers could be considered for use in capacitors with improvements in their stability and density.

Phenomenological-based mathematical modeling of porous electrode processes is viewed as an integral part of engineering advanced porous materials. This detailed effort must permit the prediction of both electrical and mechanical properties by considering processing on going in each phase of the electrode (active material, conductor, binder, and electrolyte/porosity). Present capability is inadequate.

The workshop participants felt that the optimum DOE role in a new development effort would consist of managing the overall program, clarifying rules to facilitate effective joint government/industry interaction, and establishing funding priorities. The National Laboratories would assume three prime responsibilities: (1) translate and transfer existing knowledge (properties and technology) into useful results, (2) assist industry with commercialization of existing and new technology through consultation, and (3) perform basic science and engineering (sponsoring directly by DOE) that includes the development of the phenomenological/predictive mathematical models.

METAL FOAMS

Moderators: Donald Graham and Edward Joyce

The "Metal Foams" Workshop group included nine participants, with five representatives from industry and four representatives from national laboratories. The industries represented included the paper products industry, the industrial gas separation industry, a manufacturer of macro porous metal and ceramic foams, and a research firm with focus toward (CVD) coatings. Two of the participants were from sponsoring labs and two represented other National Laboratories, however each of these individuals, attended with specific technical objective rather than as administrators of the expo.

The participants of the "Metal Foams" Workshop started with the task of reaching consensus regarding the definition of this class of product or technology. Due to the adversity of technical applications and differing objectives of the individual participants, it became clear that the definition of "Metal Foams" be very broad and inclusive rather than exclusive and narrowly limiting.

The topic of Metal Foams was defined to include an extremely wide range of porosity levels from as low as 5% or less to as great as 98% of volume. Similarly, an extremely wide pore size range was defined as acceptable with examples of macro size defined by measurement units of meters (or kilometers) to nano scale porosity measured in angstroms. It was agreed that such porosity had to be produced by deliberate intent as a desirable physical condition, rather than by accident and as a detriment to physical properties. It was agreed that a "metal foam" required the presence of a minimum, of two phases as follows: A- Solid metal phase. B- Gaseous Phase. These two phases will be interlocked throughout the physical body. It was agreed that the metal phase must be continuous throughout the structure but that the gaseous phase may or may not be continuous. This provides for the inclusion of both open cell and close cell porosity and structures.

The group proceed by indicating application preferences for metal foams as follows: Nano-scale semi-conductors; gaseous, separation, capture and storage; metal foam support matrices for coatings, (i.e. catalysis/reactors); electro/chemical devices, battery electrodes; foam noble metals in the 1 micron to 10 micron pore size ranges.

The participants identified two key physical properties required in order to perform successfully: (1) The ability to withstand cyclic or pulsating stress loads at high temperatures and high pressures without structural failure. (As compared to organic or polymer foam structures.) (2) The need to maximize ratios of modulus/density values for optimum structural support capability. The optimization of these two properties was defined as a desirable technical objective for industrial or national laboratory focus.

The "metal foams" workshop participants acknowledged the educational content of the expo's presentations as well as additional exposure and discussions regarding metal foam technologies with other expo attendees. It was agreed that few individuals or companies were aware of the full range of porous foam materials (metals) and technologies available through the National Laboratories, Universities or Industrial Manufacturers. The dis-

cussion evolved to defining the role that the DOE National Labs could take in assisting in technical development of metal foams technology.

The participants agreed that DOE and the National Labs should continue to sponsor forums such as this "Porous Materials Expo" for the exchange of information with greater publicity to industry. The majority of industrial attendees had been advised of this meeting by circulation of Expo flyers by colleagues involved in ceramics technologies. It was agreed that through meetings of this type and with higher visibility publication, industrial participants would develop higher levels of knowledge regarding metal foams and porous material technologies. Only then would industrial participants be able to identify specific technologies requiring further technical development by DOE and/or the National Labs.

MECHANICS AND RHEOLOGY

Moderators: Bhaskar Velamakanni and Andy Kraynik

The mechanics and rheology of engineered porous materials impacts the economic competitiveness of all industrial sectors- porous materials are useful because of their mechanical behavior. However, mechanics plays a much broader role in the development of porous materials than ultimate property determination because these properties depend upon pore-level structure that evolves during processing. This processing involves the flow of complex materials, such as particulate suspensions and polymeric solutions and melts, whose rheology may change with time. Industrial needs for structure-property-processing relations also include the development of non invasive characterization techniques to evaluate the evolution of mechanical properties and structure during processing. Beyond the mechanics and rheology of porous materials, industry also needs to understand mechanical and rheological behavior of complex fluids within a porous medium. Developing the ability to scale pore-level transport processes to larger scales involving different physical mechanisms offers another significant challenge that may lead to revolutionary applications of porous materials.

We believe that the Department of Energy can help convey the fundamental importance of mechanics and rheology to the field and significantly impact technological development by promoting a Center for the Mechanics and Rheology of Engineered Porous Materials that would foster collaboration at all levels. This national facility should involve a critical mass of people and contain state-of-the-art characterization equipment to serve as a resource for researchers from industry, universities, and national laboratories. The center should address generic issues that relate to all industrial sectors and also facilitate the development of local expertise to address more specific issues. The equipment and expertise concentrated at this national facility would be promoted by conducting workshops at the center.

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EXPO Agenda

ENGINEERED POROUS MATERIALS

EXPO 93

AGENDA

TUESDAY– MAY 4, 1993

1:00-4:00 pm

Tours of the Advanced Materials Laboratory

5:00-7:00 pm

Registration/Reception
Enchantment Ballroom

Participants will be given badges at registration/check-in and must wear them at all times during the conference.

ENGINEERED POROUS MATERIALS

EXPO 93

WEDNESDAY— MAY 5, 1993

7:15-8:00 am

CHECK-IN/Coffee Service

8:15 am

Welcome
Pavillon IV & V

8:30 am

Charge To Participants

8:45 am

Industrial Requirements for
Porous Materials

9:15 am

Overview of Microporous
Materials for Gas Separation

10:00 am

BREAK

10:15 am

Materials Requirements
For High Value Separations

10:45 am

Organic Aerogels

11:15 am

Complex Fluids Research for
Industrial Implications

12:15 pm

LUNCHEON: Working with the
National Laboratories
Pavillon VI

1:30 pm

Cross-linked Polystyrene Foams
Pavillon IV&V

2:00 pm

Micro and Macro-Structural
Design of Ceramic Membranes

2:30 pm

Sol-Gel Films for Energy-Related
Energy-Related Applications

3:00 pm

BREAK

3:30 pm

Microstructural Design of Foams

4:00 pm

Nanostructure Engineering of
Complex Materials

5:30 pm-
10:00 pm

POSTER SESSION

BANQUET

6:30 pm

Pavillon IV-V

Pavillon Court

Dale Schaefer, Sandia National Labs

Charles Sorrell, Dept. of Energy, AICD

John Short, JCP Co.

Charles Coe, Air Products Corp.

Pavillon Court

Vinay Goel, Millipore

*Richard Pekala, Lawrence Livermore
National Laboratory*

*David Weitz, Exxon Research &
Engineering Co.*

Kay Adams, Los Alamos National Lab

Paul Apen, Los Alamos National Lab

Phil Hsieh, Alcoa

Al Hurd, Sandia National Labs

Pavillon Court

Jim Aubert, Sandia National Labs

Dale Schaefer, Sandia National Labs

Pavillon VI

*US Senator Jeff Bingaman, New Mexico
(invited)*

* Today's meetings will be held in Pavillon IV and V unless otherwise noted *

ENGINEERED POROUS MATERIALS

THURSDAY— MAY 6, 1993

EXPO 93

7:45 am

Coffee Service

Pavillion Court

8:15 am

Characterization/Foreign
Status Report
Pavillion VI

*Douglas Smith, UNM/NSFCenter
for Micro-Engineered Ceramics*

8:45 am

Introduction to Workshops

Cliff Renschler, Sandia National Labs

9:00 am

Workshops
Fiesta Room, Enchantment Ballroom, Boardrooms North/East, Pavillion VI

Gas Separation

*Doug Fain, K25
Paul Ries, Dow Chemical*

Catalysis and Fuel Cells

*Alan Sylwester, DOE/Sandia National Labs
Len Marianowski, Inst. of Gas Technology
Gary Carlson, Sandia National Labs*

Ion Exchange

*Bob Albright, Rohm & Haas
Howard Stephens, Sandia National Labs*

Foams

*Bob Turner, Dow Chemical
Jim Wang, Sandia National Labs*

Environmental Materials

Paul Apen, Los Alamos National Labs

Insulation

*Art Yang, Armstrong World Industries
Arian Hunt, Lawrence Berkley Lab*

Sensors

Greg Frye, Sandia National Lab

Storage & Adsorbents

*Bill Earl, Los Alamos National Lab
James Wegrzyn, Brookhaven National Labs*

Batteries

*George Blomgren, Eveready
Jeff Braithwaite, Sandia National Labs*

Metal Foams

*Donald W. Graham, Astro Met, Inc.
Edward Joyce, Los Alamos National Lab*

Mechanics & Rheology

*Bhaskar Velamakanni, 3M
Andy Kraynik, Sandia National Lab*

10:00 am

BREAK

Pavillion Court

10:15 am

Workshop Reports
Enchantment Ballroom

Cliff Renschler, Sandia National Labs

11:45 am

DOE Perspective on
Expo 93
Enchantment Ballroom

Denise Swink, Dept. of Energy

12:00 pm

Closing

Dale Schaefer, Sandia National Labs

1:00-4:00 pm

Tours of the Advanced Materials Laboratory
Meet at hotel registration desk

EXPO Attendees

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R. L. Wisner	Dow North America	2030 Bldg. Midland MI 48674	517-636-9785
Dr. Yoldas	PPG Industries Technical Ctr., Chemicals Grp.	440 College Park Dr. Monroeville PA 15146	412-325-5173 412/325-5105

EXPO Attendees:ENGINEERED
POROUS
MATERIALS**EXPO 93**

Name	Organization	Address	Work Phone/FAX
Bill Ackerman	UNM/NSF Center for Ceramics	FEC 203 Albuquerque NM 87131	505-277-1621 505-277-1024
Dr. Kay Adams	Los Alamos National Laboratory Indus. Partnership Ctr.	MS 899 Los Alamos NM 87545	505-665-9090 505-665-3164
Robert L. Albright	Rohm & Haas Corporation	727 Norristown Rd. Springhouse PA 19477	215-641-7327 215-283-2555
Julie Anderson	UNM/NSF Center for Ceramics	FEC 203 Albuquerque NM 87131	505-277-3163 505-277-1024
Peter Angelini	Martin Marietta Energy Systems	Oak Ridge TN 37830	615-574-4565 (615) 574-6098
Paul Apen	Los Alamos National Laboratory Polymers & Coatings Group, MST-7	MS E549 Los Alamos NM 87545	505-665-7513
Charles Arnold	Sandia National Laboratories Div. 1811	PO Box 5800 Albuquerque NM 87185-5800	505-844-8728 505-844-9624
Dr. Assink	Sandia National Laboratories Div. 1812	PO Box 5800 Albuquerque NM 87185-5800	505-844-6372
James Aubert	Sandia National Laboratories Div. 1815	PO Box 5800 Albuquerque NM 87185-5800	505-844-4481 505-844-9624
Keith Baker	Allied Signal Inc. Bendix Kansas City Dept 814 XD44	2000 E. 95th Street Kansas City MO 64131-3059	816- 997-3698
Kenneth Balkus Jr.	University of Texas-Dallas Department of Chemistry	PO Box 830688 Richardson TX 75083-0688	214 690-2659 214 690-2925
Jon F. Bauer	Schuller International	MTC-P.O. Box 625005 Littleton CO 80162	303-978-5019 303-978-3123
Gregory Beaucage	Sandia National Laboratories Div. 1815	PO Box 5800 Albuquerque NM 87185-5800	505-1225
David J. Beecy	US Department of Energy Fossil Energy	FE-14, GTN Washington DC 20545	301-903-2693
Brian Benicewicz	Los Alamos National Laboratories MS E549, MST-7	PO Box 1663 Los Alamos NM 87545	505-665-0101 505-667-8109
George Blomgren	Eveready Battery Co.	PO Box 45035 WestLake OH 44145	216-835-7757
Ulrich Boes	Cabot Corporation	157 Concord Road Billerica MA 01821	508-670-6209 508-667-7152
Tony Bottone	Quantachrome	9575 Paseo Monril San Diego CA 92129	619- 484-0145 (619) 484-0145
Rasto Brezny	W.R. Grace & Company	7379 Route 32 Columbia MD 21044	410-531-4551 410/531-4767
Eileen Buckley	Corning Inc.	Main Plant 21-0113 Corning NY 14831	607-974-4170 607-974-4073
James M. Bunch	Los Alamos National Laboratory WX5	Los Alamos NM 87545	505-667-6043 505-667-5782
David Calabro	Mobil Res & Dev. Corporation Central Research Laboratory	PO Box 1025 Princeton NJ 08540	609-737-4102 609/737-5217

Advanced Materials Laboratory Tour

Sandia National Laboratories

Albuquerque, New Mexico 87185

date: May 6, July 20, 1993

to: Dale Schaefer, 1703

from: Gary Carlson, 6211 Acting

subject: AML Tours in Connection with Engineered Porous Materials Expo

I am pleased to report that roughly 55 persons toured the AML during the Engineered Porous Materials Expo (~10 on May 4th and ~45 on May 6). I received feedback that the tours were very well-received and contributed significantly to the participants' meeting experience. I would especially like to single out and thank Mary Russo for helping me to organize the tours, and Ron Loehman, Joe Cesarano and Kevin Ewsuk for conducting the tours. Thanks very much for your extra effort and fine work!

Copy to:

1700 Bob Eagan
1708 Ron Loehman
1708 Mary Russo
1841 Alan Hurd
1841 Joe Cesarano
1841 Kevin Ewsuk
6211 Gary Carlson

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