Lawrence Livermore Laboratory

LOW-DENSITY, SALT-LOADED FOAMS

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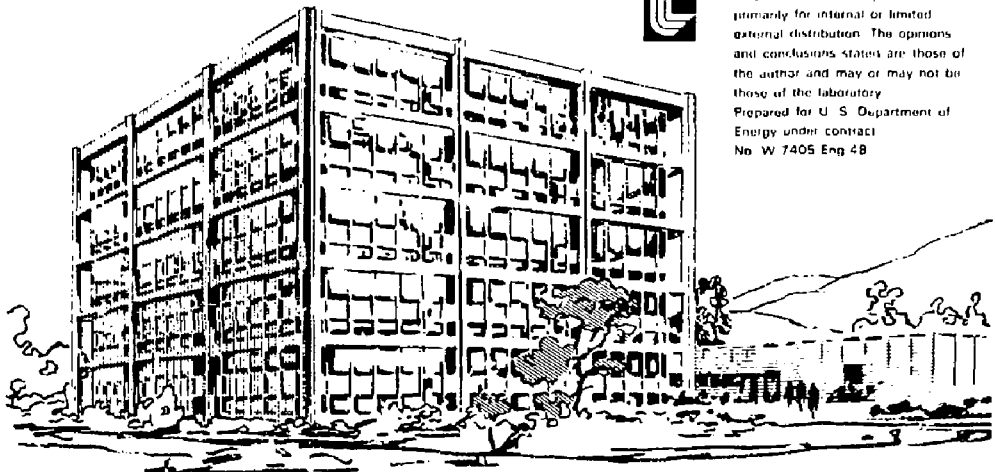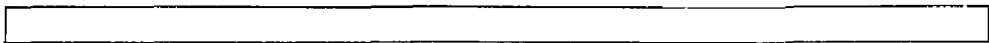
ABSTRACT

An experiment was conducted at LLL that required low-density, fine-celled foams uniformly loaded with rubidium. Foams meeting these requirements were produced by impregnating foams made from polyacrylonitrile $(C_3H_3N)_n$ with rubidium fluoride. Foams with densities from 0.075 to 0.4 g/cm³ were prepared and loaded with .002 to 0.20 g/cm³ of rubidium fluoride.

INTRODUCTION

... (illegible) ... Foams also can be ... (illegible) ... The limiting factors are (1) density of the foam without rubidium, (2) size of small cells ... presumably less than 65 μm, (3) rubidium density and uniform rubidium distribution, and (4) uniformity, straightness, and strength of the tube-shaped cylinders.

CELL FORMATION PROCESS

The cell formation process by which a polymer solution is transformed into a polymer gel with a fixed cell structure is outlined in detail by W. Wrasidlo.[3] Briefly, polymers solidify by spinoidal decomposition or by nucleation and growth. In spinoidal decomposition, a polymer in solution solidifies to form an interpenetrating network — a gel. This may occur either in solution when long-chain molecules associate to form entanglement networks or when the

solvent is evaporated to cause supersaturation (i.e., the equilibrium polymer-rich phase grows into the solvent phase). Because spinoidal decomposition occurs with diffuse boundaries (surfaces are *not* made), interpenetrating networks are formed.

In cases where there is not enough supersaturation to cause phase separation, solidification may occur by nucleation and growth. The nuclei are supplied by the polymer-rich portion of the interpenetrating network. Growth takes place to form columnar structures and continues until the growth rate of the column exceeds the diffusion rate of the solvent. After a critical columnar length is reached, the growth rate decreases until the solvent diffusion rate reaches a high enough value to reinitiate the growth. However, because more time is required for the solvent to reach the new layer of polymer, the columns become longer and wider.

These general processes have been observed in the formation of both PAN and CA foams. Spinoidal decomposition yields foams with uniform micrometer-sized cells; nucleation and growth yields foams with columnar cells. Either mechanism of polymer solidification can be selected by adjusting the solvent system and the temperature of solidification.

EXPERIMENTAL PAN FOAMS

The process for making salt-loaded PAN foams consists of five basic steps:
(1) Preparation of the PAN solution.
(2) Molding or extrusion of a polymer gel rod.
(3) Soaking the gel rods in rubidium fluoride solutions.
(4) Solvent transfer to remove water.
(5) Freeze drying.
Each step is discussed below.

PAN Solution Preparation

For uniform, isotropic, micrometer-sized cells, the polymer solution must be close to precipitation. That is, the polymer must be dissolved in a solvent or solvent mixture that barely dissolves the polymer. When this solution is extruded into a nonsolvent, the polymer phases out of solution rapidly (spinoidal decomposition) and forms small, uniform, open cells. If the solvent used to prepare the polymer solution is too good (i.e., readily dissolves the polymer), columnar cells form by nucleation and growth.

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Examples of these two types of foam cell structures are shown in Fig. 1.
Figure 1a is a photograph of the cross section of a foam cylinder, showing
the large linear cells produced by extruding a 3 wt% solution of PAN (Aldrich
Chemical Co. #18, 131-5) dissolved in N,N-dimethylacetamide (DMA) into room
temperature water. The foam shown in Fig. 1b was produced from the same 3 wt%
solution of PAN in DMA to which about 5 to 10% acetone had been added. The
addition of the acetone, a nonsolvent for PAN, reduces the solvent power of
DMA and changes the polymer solidification process from nucleation and growth
to spinoidal decomposition.

Several variables can be adjusted to vary the foam cell size; the addition
of acetone appears to be the most effective. The temperature of the water bath
(or methanol/water bath) into which the polymer solution is extruded also
affects the foam cell size. Uniform, submicrometer-sized cells can be produced
by extruding the PAN/DMA/acetone solution into 0°C water.

A 3 to 3.5 wt% solution of PAN in DMA/acetone yields foams with densities
of 0.05 to 0.06 g/cm^3. Solutions of 2 wt% PAN are too low in viscosity to
extrude well. Solutions of 4 and 5 wt% PAN are too viscous, making it diffi-
cult to prepare uniform solutions. At the higher PAN concentrations, dimethyl
formamide is a better solvent because it yields less viscous solutions.

To prepare a 3 wt% solution of PAN in DMA/acetone, we used the following
procedure. The polymer is dissolved in the DMA, with stirring, by heating
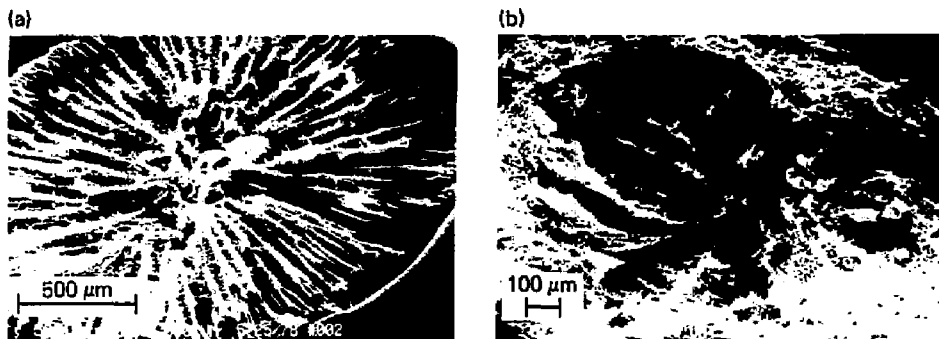

Fig. 1.   Photomicrographs of polyacrylonitrile (PAN) foam: (a) foam formed
by nucleation and growth (density = 0.06 g/cm^3), note the columnar
cell structure; (b) foam formed by spinoidal decomposition (density
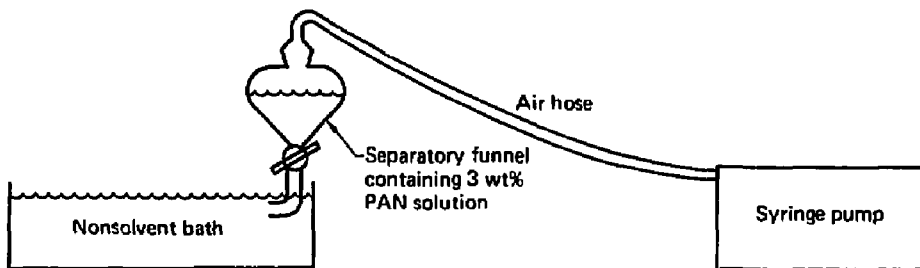= 0.065 g/cm^3), note the ~10-µm diameter isotropic cells.

Fig. 2. Diagram of the PAN extrusion apparatus.

the solution to 90°C in a closed container (no air). Overheating results in
polymer decomposition (evidenced by a brown solution) with a much lower
viscosity. The solution is cooled to room temperature and the acetone is added
slowly with stirring until the solution clouds and then clears with further
stirring.

Extrusion or Molding of Polymer Gel Cylinders

We evaluated two methods for fabricating the polymer cylinders. The
molding technique consists of filling a glass tube (5 to 10 cm in length and
1 to 3 mm i.d.) with the polymer solution and placing it horizontally in a
water bath. By diffusion, water forces the polymer out of solution and a
gelled cylinder is formed. This process has two drawbacks: (1) the diffusion
time is long (1 to 3 weeks) for complete separation, and (2) the gel diameter
generally is irregular and only short pieces of uniform-diameter gel are
obtained.

In the extrusion process for making gel cylinders, we tried several
variations, including vertical and horizontal extrusion, different nonsolvents
(generally water or methanol/water), different temperatures of the nonsolvent,
and density gradients in the nonsolvent when extrusion is done in a vertical
position. In the most successful method, extrusion is carried out with the
extrusion orifice in a horizontal position. The polymer solution is forced
from the orifice under constant pressure into a 0 to 55°C water bath or into
a methanol/water bath with a density of approximately 0.94 g/cm^3. Figure 2
diagrams this experimental apparatus.

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The syringe pump provides a constant driving force to expel the polymer solution from the orifice; a 4 to 8 cm^3/min rate generally is used. A glass orifice (2.4 mm i.d.) is attached to the bottom of a separating funnel that is fitted with a hollow standard taper stopper. A flat 25 by 32 by 10 cm tray holds the nonsolvent. In operation, the syringe pump is started and the valve is opened to start the extrusion. As the polymer solution extrudes, it must be guided to form a straight cylinder and must be kept below the surface of the nonsolvent liquid surface. Because of surface tension effects, we normally add a small amount of soap to the nonsolvent. After a gel cylinder 10 to 20 cm long is extruded, it is cut off and another rod is extruded. The freshly extruded rods float for 1 to 3 min before sinking to the bottom of the tray. They are allowed to soak in the nonsolvent for 0.5 to 2 h to complete the polymer separation and to allow the solvent molecules to diffuse out. The rods are then transferred to pure water for additional soaking. Finally, they are freeze-dried to produce unloaded foams or placed in a salt solution to produce salt-loaded foams.

Rubidium Fluoride Loading

To impregnate the PAN gel rods with rubidium fluoride, or any other water soluble salt, they are soaked in a solution of 0.03 to 0.2 g/cm^3 RbF for several hours to ensure uniform salt distribution. Solutions of 0.05 g/cm^3 RbF yield RbF densities of 0.05 g/cm^3 in the final foam, if salt is not lost in the solvent transfer step and if shrinkage is minor.

Solvent Transfer

After the PAN gel rod is impregnated with RbF, it must be freeze-dried to produce a low density foam. If the gel rod is removed from the RbF solution, frozen and freeze-dried, a high density (>0.2 g/cm^3), shrunken, and distorted rod is obtained. To produce a uniform, low-density foam, the water in the gel (a polar liquid) must be replaced by a nonpolar liquid before freeze-drying. To do this, the rod is first soaked in methanol (for 10 to 30 min) to replace the water, then in acetone (to replace the methanol), and then in benzene. Each of these solvents is less polar than the previous one and is misable with the solvents on either side.

When the gel rods contain RbF, the process must be modified to prevent the loss of the RbF. In this case, the solvents — methanol, acetone, and

benzene — must be saturated with RbF before the solvent transfer is begun.
While the solubility of RbF in these pure solvents is low,[4] it is significantly
higher when water is present. This is the case when the gel rod is transferred
from the RbF/water solution into methanol.

Freeze Drying

The gel cylinders are freeze-dried to produce the foam rods. Several
methods of solvent removal other than freeze-drying have been attempted (e.g.,
air-drying), but all cause excessive shrinkage. In the technique we now use,
gel rods with or without RbF are removed from benzene and placed in "V" blocks
to maintain straightness and covered with a porous metal plate to prevent
vertical distortion. The gel rod in the "V" block is placed in a bath of
hexanes at -50 to -70°C for a few minutes and then transferred to a vacuum
chamber for 4 to 10 h to complete the freeze-drying. Pressures of 5 to 60 μm Hg
are used in our experiments.

RESULTS

PAN Foams without RbF

Foams of PAN were prepared with densities ranging from 0.05 to 0.4 g/cm^3;
most foams had densities of 0.05 to 0.1 g/cm^3 because this was the range of
interest. Extruded foam cylinders had diameters from 1.7 to 3.0 mm and molded
foams had diameters from 1 to 2.2 mm. These diameters represent the range of
foams produced, not the limits of the fabrication techniques. Figure 3 is a
photograph of a sample foam cylinder. Note the absence of any apparent surface
cell structure and the uniformity of the foam diameter, generally ±0.1 mm.
In Fig. 4, we present several SEM photomicrographs at magnifications of 65 to
10,000× to illustrate the cell structure of a 0.05-g/cm^3 PAN foam molded in
a glass tube and phase-separated with water. This type of cell structure is
typical of these fine-celled foams. Examination of the 10,000× photomicrograph
reveals that the foam structure consists of columns and webs with dimensions
of 0.1 to 0.5 μm i.e., the foam is open celled.

A different cell structure is formed when the PAN/DMA/acetone solution is
extruded into the methanol/water bath. In this case, a fine-celled foam is
still formed; however, the texture is considerably different (see Fig. 5).
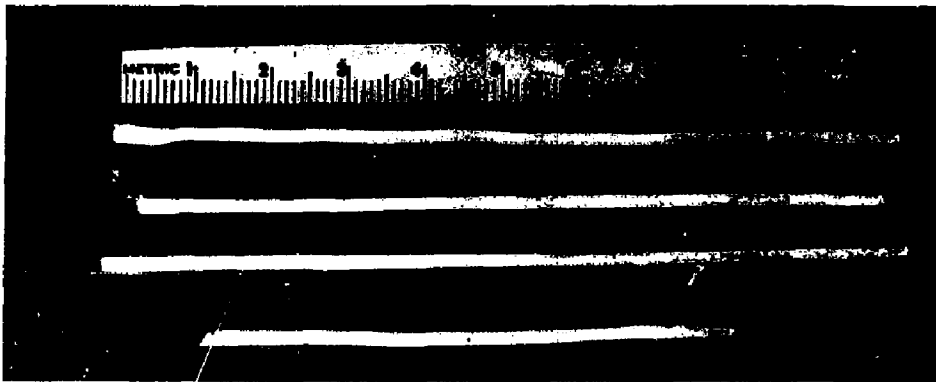This foam has a density of 0.08 g/cm^3. It appears grainy with small pores

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Fig. 3. Photograph of four PAN foam rods, 2 mm in diameter. These rods contain
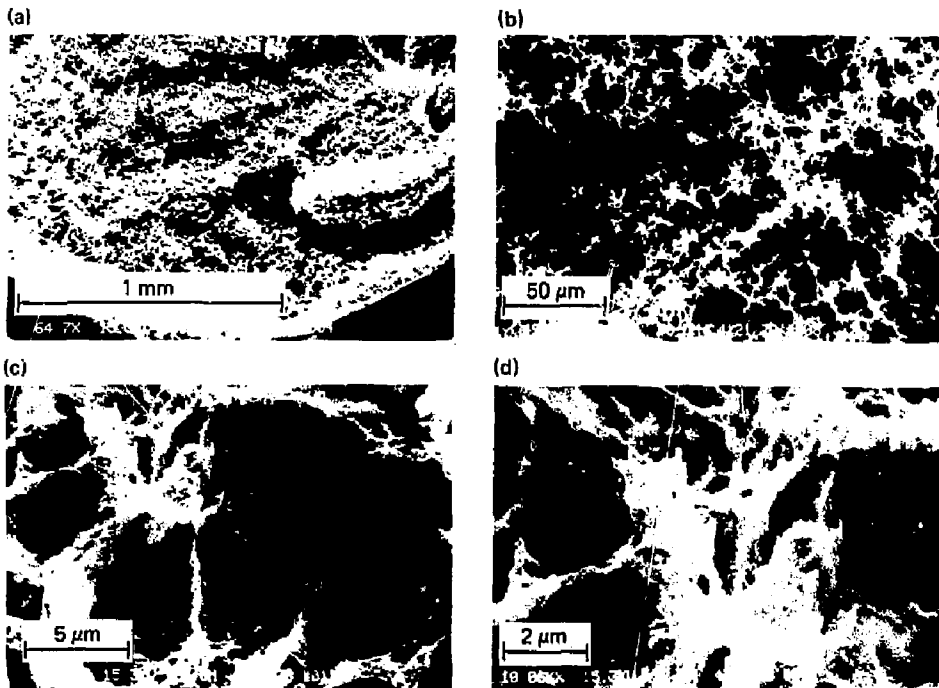0.05 g/cm^3 RbF in a PAN foam of 0.05 g/cm^3, for a total density of
0.1 g/cm^3.

(a)

(b)

(c)

(d)

Fig. 4. Scanning electron microscope photographs of a 0.05-g/cm^3 PAN foam at
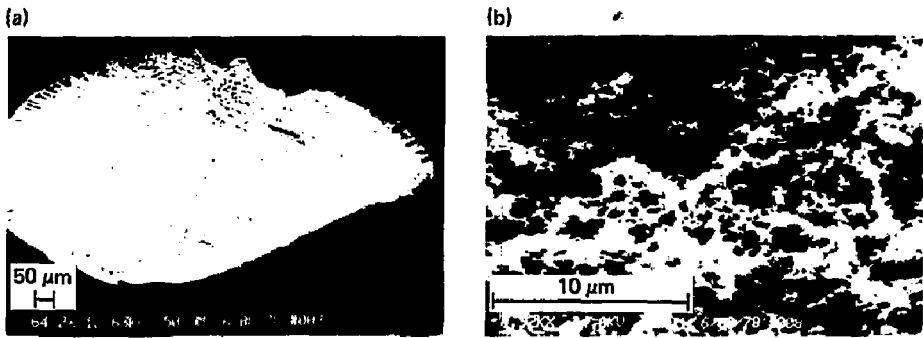increasing magnification: (a) 64.7×, (b) 499×, (c) 5000×, and (d)
10,060×.

Fig. 5. Photomicrographs of PAN foam showing the grainy cell structure pro-
duced by extrusion into a methanol/water bath (foam density = 0.07
g/cm^3): (a) 64.2×, (b) 4920×.

Fig. 6. Energy dispersive x-ray analysis of a PAN foam cylinder in cross
section, edge to center. The peak at 1.69 Å is due to the rubidium.

~1 µm in diameter. Also, there is a layer about 50 µm thick of large cells around the outside of this foam cylinder. The cause of this layer is unknown at this time, but probably is related to the extrusion process.

Foams Containing RbF

PAN foams with densities of 0.05 to 0.1 g/cm^3 were loaded with 0.04 to 0.20 g/cm^3 of RbF. The main concerns with the RbF-loaded foams were the RbF concentration, the uniformity of its distribution, and the physical properties of the loaded foam. Concentrations of RbF in the foam ranged from 8.4 to 81.5 wt%; actual RbF concentrations were confirmed by analytical chemistry. Because RbF is deliquescent (i.e., it absorbs moisture on exposure to ambient air), it must be protected at all times. Moisture absorption for foams containing 0.1 g/cm^3 RbF range from 10 to 20%. RbF-loaded foams that have absorbed moisture are sticky and difficult to handle.

The distribution of RbF within a foam cylinder was determined by energy dispersive x-ray (EDX) analysis. With this technique, the cross section of a fractured foam cylinder is examined in four locations from the edge to the center for x-rays emitted by rubidium. Figure 6 shows four of these scans. The peak at 1.69 Å is due to rubidium. The other peaks are caused by the gold used to coat the SEM sample. These curves clearly show that the rubidium is uniformly distributed to within an uncertainty of about ±10%. The sample used for the EDX analysis contained 0.2 g/cm^3 RbF and gives a good visual indication of the RbF distribution (see Fig. 7). At 500× (Fig. 7a), the foam cell structure appears normal with no sign of RbF crystals or powder. The photograph at 500× (Fig. 7b) reveals that the RbF coats the cell structure (compare with Fig. 4) and the RbF distribution is therefore a function of the foam cellular geometry.

CONCLUSIONS

PAN foams with and without added salts can be produced (1) at low densities, (2) in the form of long cylinders 1 to 3 mm in diameter, and (3) with variable cell structures. Foams also can be produced as thin sheets and square cross section rods. Loading of up to 0.2 g/cm^3 (81 wt%) RbF was achieved; higher loadings are possible. Foams with a density of 0.05 g/cm^3 are soft and difficult to handle. Strength increases rapidly with an increase
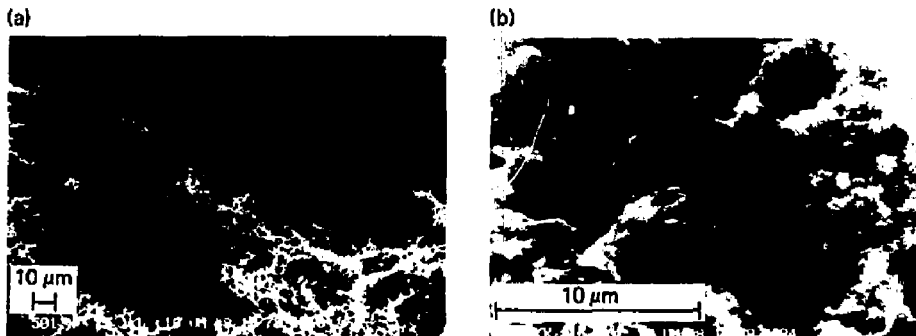
Fig. 7. Scanning electron microscope photographs of a 0.05-g/cm^3 PAN foam loaded with 0.2 g/cm^3 RbF: (a) 501×, (b) 5050×.

in foam density. Also, the strength of foam with columnar cells is higher than that of foam with small isotropic cells.

ACKNOWLEDGEMENTS

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