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In many experimental studies using porous materials it is desireable to have highly regular pore structures where the local porosity and specific surface area are determinable to a much greater accuracy than would be possible with random pore configurations. In these cases knowledge of the pore geometry reduces the number of unknown parameters of the system thereby permitting a more quantitative assessment of experimental results. Some investigators have used porous bodies composed of bundles of fine tubes (1) or beds of small spheres (2) to accomplish this purpose, but the former approach is limited to pores of quite large dimensions ($>300\mu$) while the latter gives structures of insufficient regularity for many purposes.

In connection with studies of anodic dissolution of porous metal electrodes a technique has been developed for fabrication of porous structures possessing highly uniform porosity and having individual pores of nearly identical and uniform size and shape (3). These structures are formed from fine wires sintered in parallel closed packed configuration.

In principle, the method may be used to fabricate porous bodies from any material which may be sintered and which is available in wire form. A bundle of straight wires is assembled in such a way that the wires lie in a hexagonal close-packed array. The bundle is then sintered under appropriate conditions of temperature and duration. The resulting mass has parallel individual pores passing through it which correspond to the original void spaces between wires. If the assembly of the bundle is carefully accomplished, all of the pores will have very nearly the same size and shape. This method of assembling wires in a hexagonal close-packed array is an extension of the work of Alexander and Balluffi(4) to the formation of porous bodies on a considerably larger scale.

Proper choice of sintering conditions will allow complete fusion of adjacent wires along lines of contact and elimination of the narrow fissures bordering these contact lines without distortion of the overall structure. An array of straight wires can be closely approximated by sections of a large wire coil where the radius of curvature of windings is much greater than any pore length of interest. This technique has been successfully applied to fabrication of porous copper electrodes with pores of about 35μ diameter.

Experimental

Porous structures were fabricated from 0.010 inch diameter copper wire (BS No. 30, 99.9% Cu) formed in a coil of 6 5/8 inch inside diameter. In order to promote good sintering conditions, the wire was first cleaned by passing it through three tricholoethylene solvent baths and winding onto a clean spool. After this procedure the wire was stored under contamination free conditions. The degreased wire was wound in hexagonal close-packed array on a stainless steel spool (6 5/8" diameter, 3 3/4" width) which was mounted on and driven by a variable speed lathe.

The coil winding apparatus, with the spool and coil in place, is shown in Figure 1. The wire passes from its feed spool, which is driven at a rate synchronized with winding speed, through the tension maintaining device diagramed in Figure 2. It then passes through a Teflon guide block which rides on a traveling support. This support is driven parallel to the coil axis by a sleeve surrounding a threaded (100 threads per inch) portion of the shaft on which the coil is mounted. In this manner the guide block is displaced laterally exactly one wire diameter per spool revolution.

The first layer of wire was wound in such a way that on each turn the wire was in contact with the neighboring wire, wound on the previous turn. Each subsequent layer of wire was wound in the same direction and placed in the crack between wires of the preceding layer. In this manner 83 layers of wire were placed on the spool (a 1.04 cm thickness). During the winding, the tension in the wire was maintained at approximately 130 grams-force.

After completion of winding, the air contained in the coil was evacuated and replaced with nitrogen. The coil was then stored in nitrogen until sintering. At that time the nitrogen was removed under vacuum and replaced with hydrogen. The coil was then placed in furnace with a hydrogen atmosphere and sintered for sixty hours at 1,050 ± 10°C. These conditions were determined by the results of test sinterings made with small coils of the same wire for temperatures of from 980°C to 1070°C and for sintering times of from 4 hours to 64 hours. After sintering the temperature was reduced at the approximate rate of 100°C/hour.

Individual porous blocks were cut from the sintered coil on a milling machine. The coil was mounted horizontally on a dividing head and cuts were made with a vertical slitting saw on a horizontal spindle. The first cut, of two used to remove a block, was made such that the exposed surface was about 0.04 cm off the plane of the axis of the coil. The second cut was made parallel to the first to give a rough piece about 0.57 cm thick. The pieces were then machined to dimension 1.4 X 5.4 X 0.5 cm using a sharp fly cutter, with the pores intersecting the 1.4 X 5.4 cm face at approximately right angles. This removed about 0.04 cm from these faces and did not damage the pore structure although it wiped or smeared a thin film of copper over the surface, largely closing over the pores. The smeared film was then removed by electrochemical dissolution in dilute sulfuric acid at current densities sufficiently high

($\sim 0.8 A/cm^2$) to prevent penetration of the reaction appreciably into the pores; about 3 minutes of such electrolysis was required to give clean surfaces with open pores.

Results and Discussion

A typical cross-section of the resulting porous structure is shown greatly enlarged in Figure 3. From photographic enlargements, measurements of individual pore cross-sectional areas and perimeters yielded mean values, at the 95% confidence level of

$$1.964(\pm 0.101) \times 10^{-5} \text{ cm}^2, \text{ and}$$

$$2.22(\pm 0.05) \times 10^{-2} \text{ cm},$$

respectively, and thus a specific surface area of

$$1{,}130 \text{ cm}^2/\text{cm}^3$$

based upon void volume. The porosity was 3.5%.

Porous materials fabricated by the method outlined above have a highly uniform porosity. This property is particularly advantageous in such applications as the study of the rate of dissolution at various locations within porous bodies. If the porosity is initially uniform, measurement of the porosity distribution throughout the porous piece after dissolution immediately gives the time-averaged reaction rate during dissolution. This type of porous body has a further advantage. Should a large part of the sintered contact region be removed by a process such as dissolution, the material will still retain its essential structure. Further, analyses of many experiments involve a parameter which contains the product of the specific surface area and the reaction rate

constant, and often neither of these is known with confidence. Thus use of porous bodies such as those described here having a known and uniform specific surface area facilitates the theoretical interpretation of experimental data. Finally, the structures formed by this method possess a regular geometry readily described mathematically. They thus lend themselves well to experimental investigation of theories based on well characterized pore configurations.

Acknowledgment

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3. R. Alkire, Reaction Distribution in a Dissolving Porous Anode, Ph.D. Thesis, UCRL-18425, Lawrence Radiation Laboratory, University of California, Berkeley, September, 1968.
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Figure Captions

Figure 1. Coil winding apparatus.

Figure 2. Schematic diagram of coil winding device.

A. Variable speed motor drive

B. Feed spool

C. Tensioning roller

D. Fixed Teflon guide

E. Low inertia drag wheel with friction brake

F. Damped spring dynamometer for tension measurement

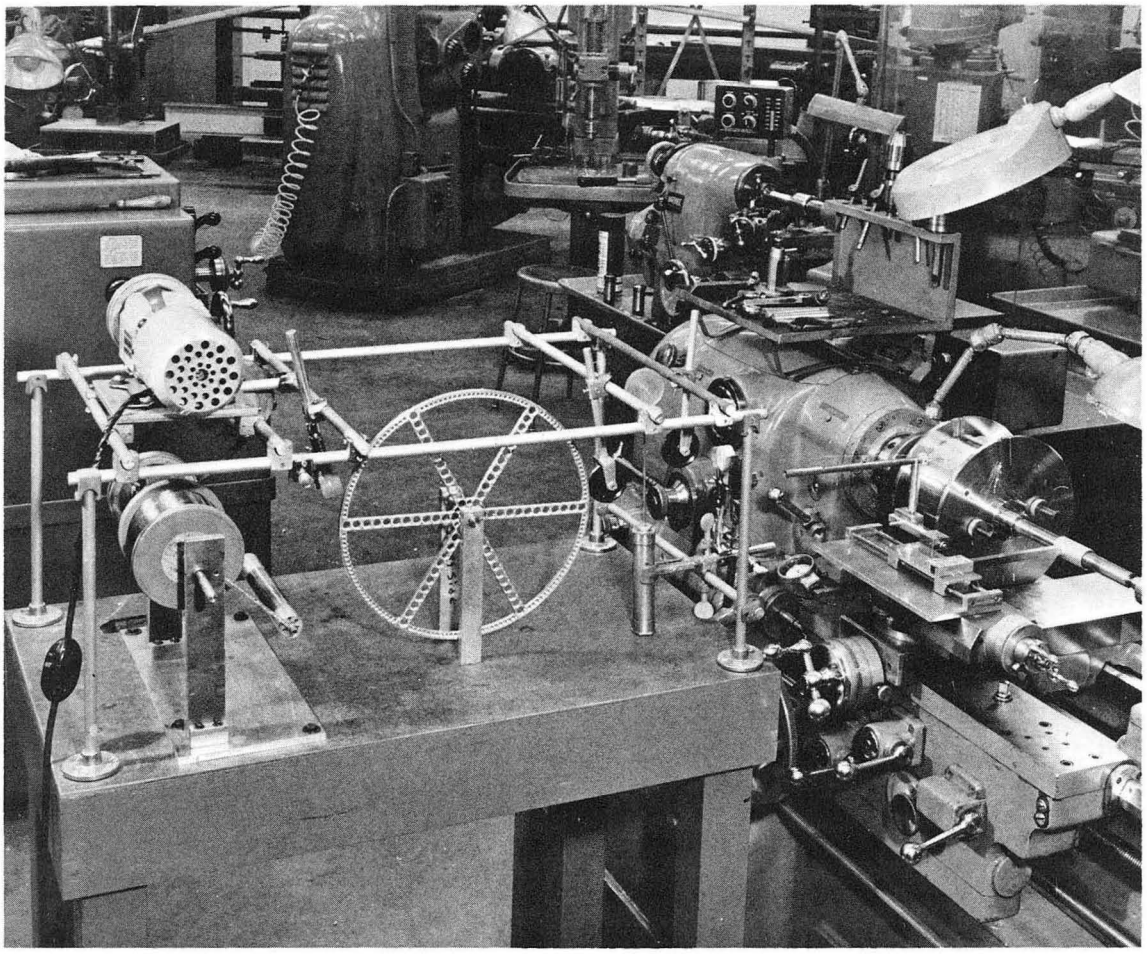
G. Traveling Teflon guide

H. Guide drive mechanism

I. Coil

Figure 3. Porous electrode structure.

Enlarged cross section parallel to electrode face.



XBB 674-2061

Fig. 1

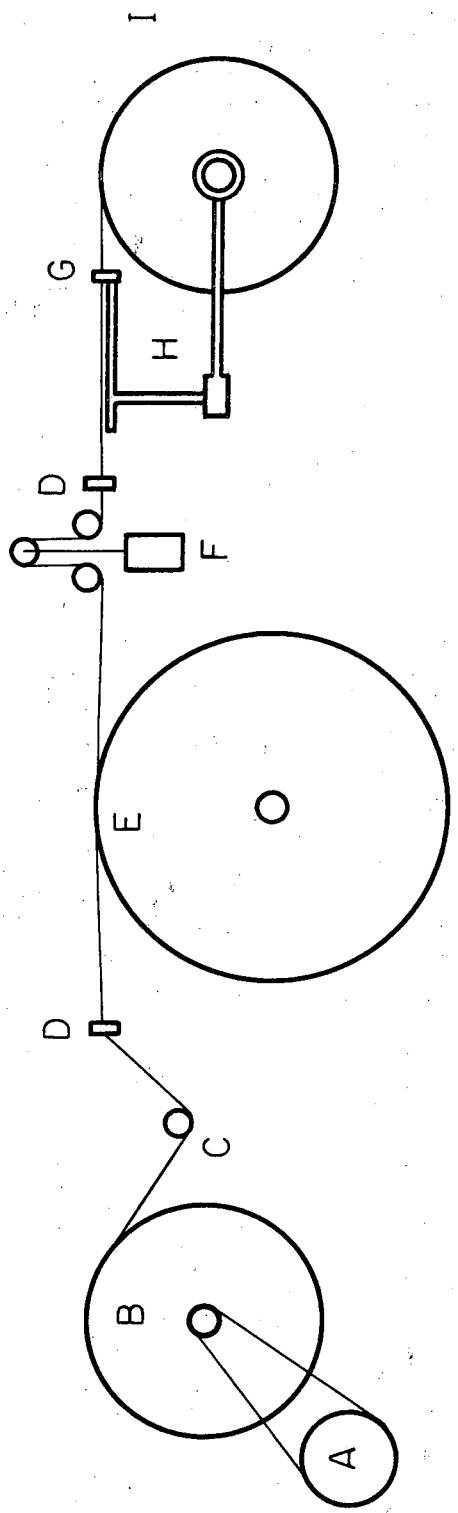


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Fig. 2

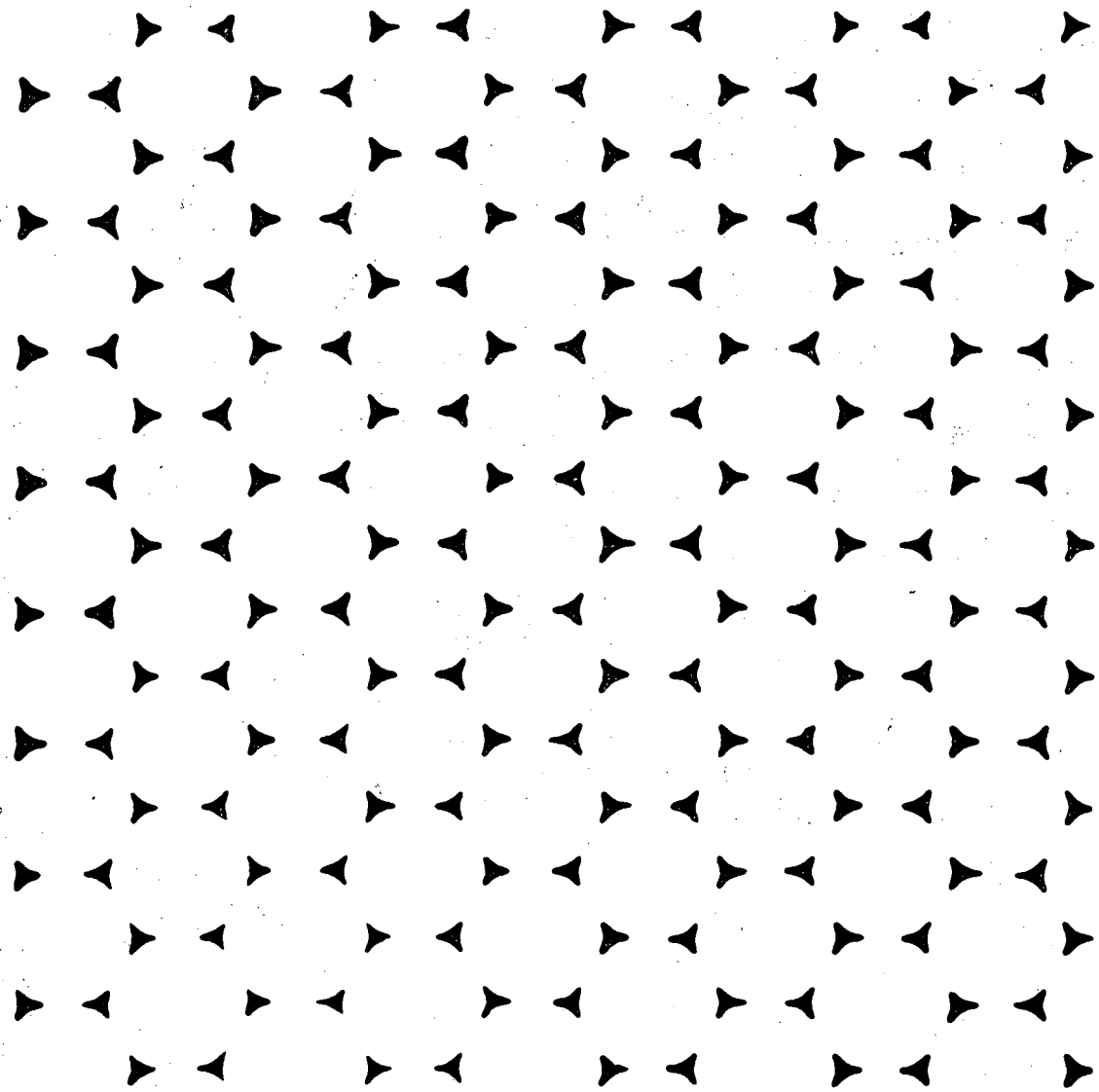

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Fig. 3

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