HOLLOW-FIBER MEMBRANES

I. Moch Jr.
I. Moch and Associates Inc., Wilmington, Delaware, USA

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Contents

Summary

Hollow-fiber membranes were invented about 30 years ago. In the ensuing decades much research and development effort has taken place with the result that these fibers have become exceedingly important to industry, academia and government in such

fields as desalination of water, wastewater reclamation, medicine, agriculture, gas separation and pervaporation. Commercial opportunities now exceed several hundred million dollars annually. The hollow-fiber membranes are usually the base technology within a significantly larger system.

This article has discussed the history and theory of hollow-fiber membrane technology. Methods of manufacture have been reviewed, together with processing techniques employed to enhance various aspects of performance. Hollow-fiber membranes are composed of many different materials of construction. The genetic compositions are cited and specific end-use applications noted. Lastly, many areas have been identified where future prospects for hollow-fiber membranes are the brightest.

1. Introduction

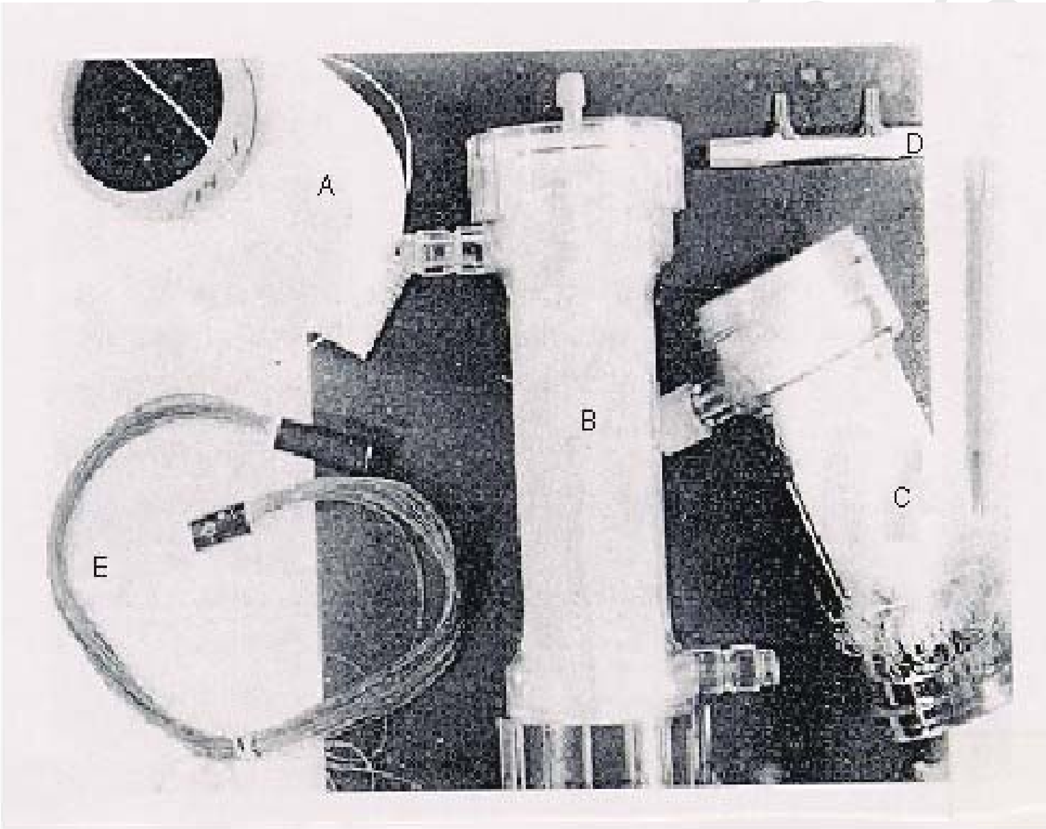

Figure 1. A, hollow-fiber spool; B, hollow-fiber cartridge employed in hemodialysis; C, cartridge identical to item B demonstrating high packing density; D, hollow-fiber assembly employed for tissue cell growth; E, hollow-fiber bundle potted at its ends to be inserted into a cartridge or employed in a situation that requires mechanical flexibility.

The development of hollow-fiber membrane technology has been greatly inspired by an intense research and development of reverse-osmosis membranes during the 1960s. DuPont pioneered with an aramid polymer device commercialized in 1969 followed by Dow Chemical Company and Toyobo (Japan) with a cellulose triacetate polymer. The excellent mass-transfer properties conferred by the hollow-fiber configuration soon led to numerous applications (Mahon and Lipps 1971). Commercial applications have been established in the medical field, in water reclamation, in gas separations and pervaporation and in various others stages of development. A hollow-fiber membrane is a capillary having an inside diameter of >25 μm and an outside diameter <1 mm and whose wall functions as a semipermeable membrane. The fibers can be employed singly or grouped into a bundle which may contain tens of thousands of fibers and up to several million fibers as in reverse osmosis (Figure 1). In most cases, hollow-fibers are used as cylindrical membranes that permit selective exchange of materials across their walls. However, they can also be used as "containers" to effect the controlled release of a specific material (Baker and Lonsdale 1974), or as reactors to chemically modify a permeate as it diffuses through a chemically activated hollow-fiber wall, e.g. loaded with immobilized enzyme.

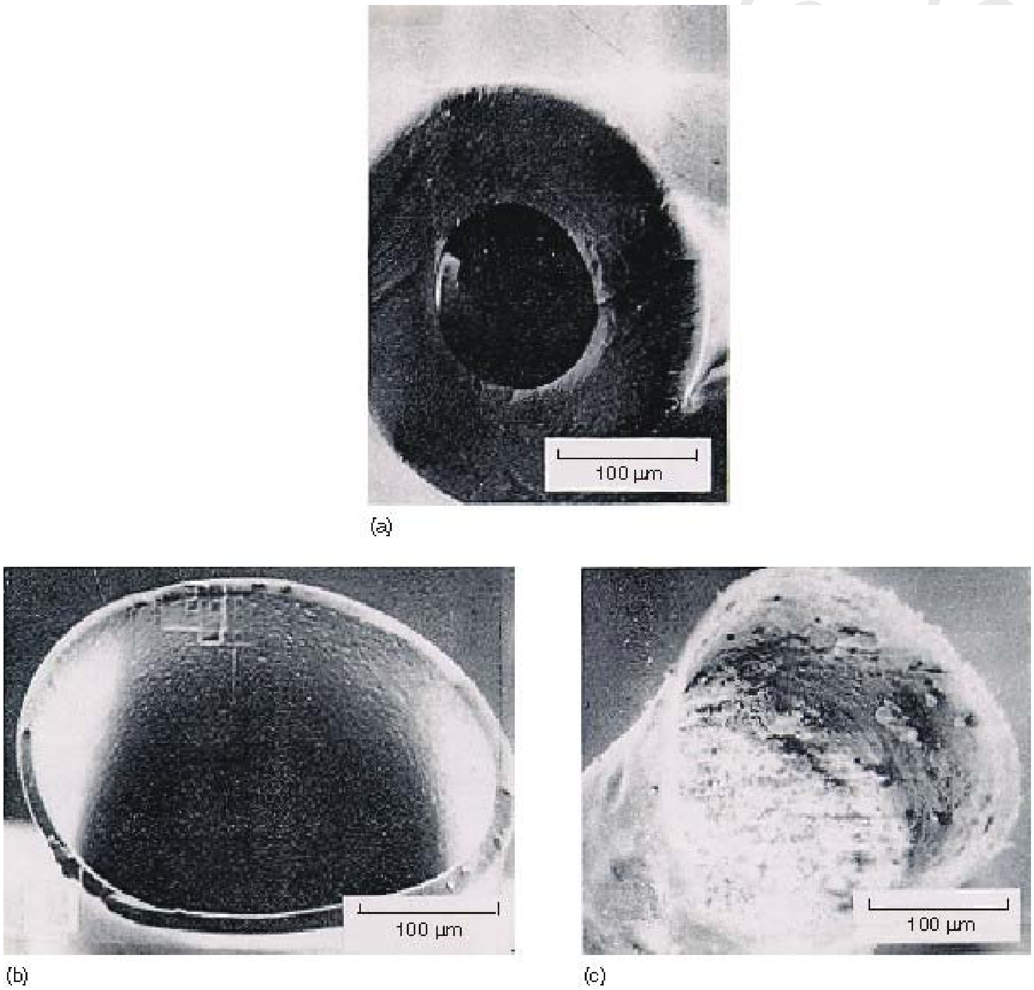

Figure 2. (a) Thick-walled hollow-fiber for high pressure desalination application; (b) thin-walled acrylic hollow-fiber; (c) sorbent-filled fiber.

Hollow-fiber membranes, therefore, may broadly be divided into two categories: "open" hollow-fibers (Figures 2a and 2b) where a gas or liquid permeates across the fiber wall, while flow in the lumen side of medium-gas or liquid is not restricted, and "loaded" fibers (Figure 2c) where the lumen is filled with an immobilized solid, liquid, or gas medium. The "open" hollow-fiber has two basic geometries: the first is a loop of fiber or a closed bundle of fibers contained in a pressurized vessel. Gas or liquid from the outer side of the fiber permeates through the fiber wall and exits via the open fiber ends. In the second type, fibers are open at both ends. The feed fluid can be circulated on the inside or outside of the relatively large diameter fibers. These so-called large capillary ("spaghetti") fibers are used in microfiltration, ultrafiltration, pervaporation and some low pressure (less than 1035 kPa) gas applications. Potential applications for the two types of hollow-fiber membranes are presented in Figure 3.

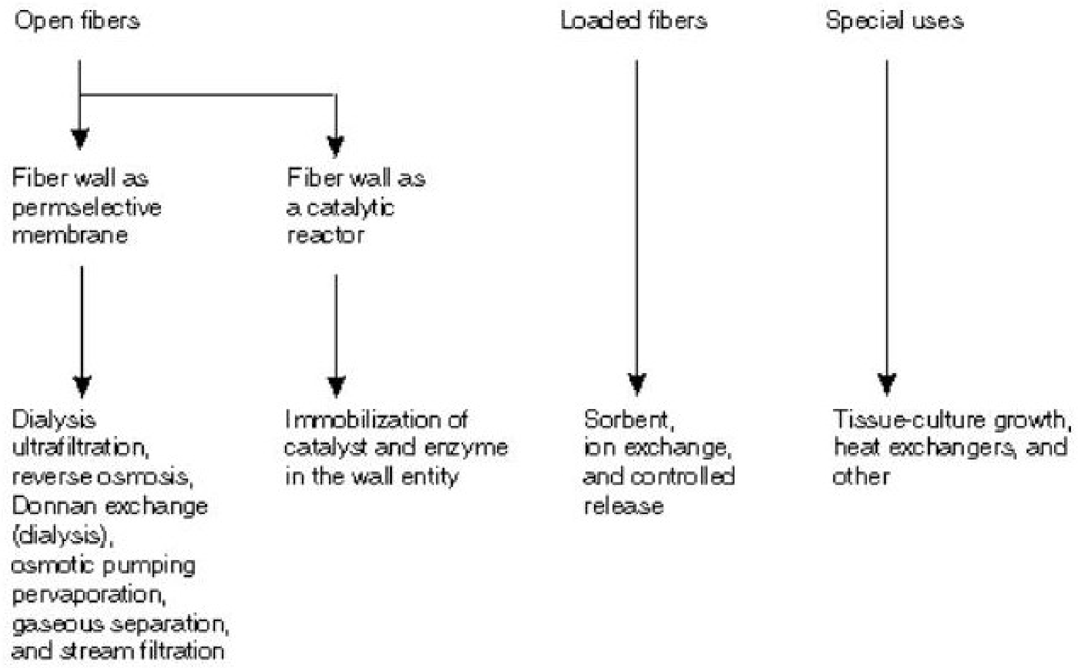

Figure 3. Hollow-fiber applications.

Hollow-fibers offer three primary advantages over flat-sheet or tubular membranes. First, hollow-fibers exhibit higher productivity per unit volume; second, they are self supporting, and thirdly high recovery in individual units can be tolerated. The high productivity is derived from a high packing density and a large surface area. Since surface area-to-volume ratio varies inversely with fiber diameter, a 0.04 m^3 membrane device can easily accommodate 575 m^2 of effective membrane area in hollow-fiber form (90 mm in diameter), compared to about 30 m^2 of spiral wound flat-sheet membrane and about 5 m^2 of membrane in a tubular configuration. Because they are self-supporting, the hollow-fiber membranes greatly simplify the hardware for fabrication of a membrane permeator. Whereas flat-sheet membranes employed in ultrafiltration or reverse-osmosis modules must be assembled with spacers, porous supports, or both, a bundle of hollow-fibers can simply be potted into a standard size tube of plastic or metal, as shown in Figure 1. The primary disadvantage of the hollow-fiber unit compared to the other membrane configurations is its sensitivity to fouling and plugging by particulate matter due to a relatively low free space between fibers as well as the small inside diameters. In commercial applications this problem is greatly lessened by designing systems with good pretreatment of feed before sending it to the hollow-fiber devices.

Hollow-fibers can be prepared from almost any spinnable material. The fiber can be spun directly as a membrane or as a substrate which is post-treated to achieve the desired membrane characteristics. Analogous fibers are spun in the textile industry and are employed for the production of high bulk, low density fabrics. The technology employed in the fabrication of synthetic fibers therefore applies also to the spinning of hollow-fiber membranes by melt or wet-spinning from natural and synthetic polymers.

2. Properties

2.1. Basic Morphology

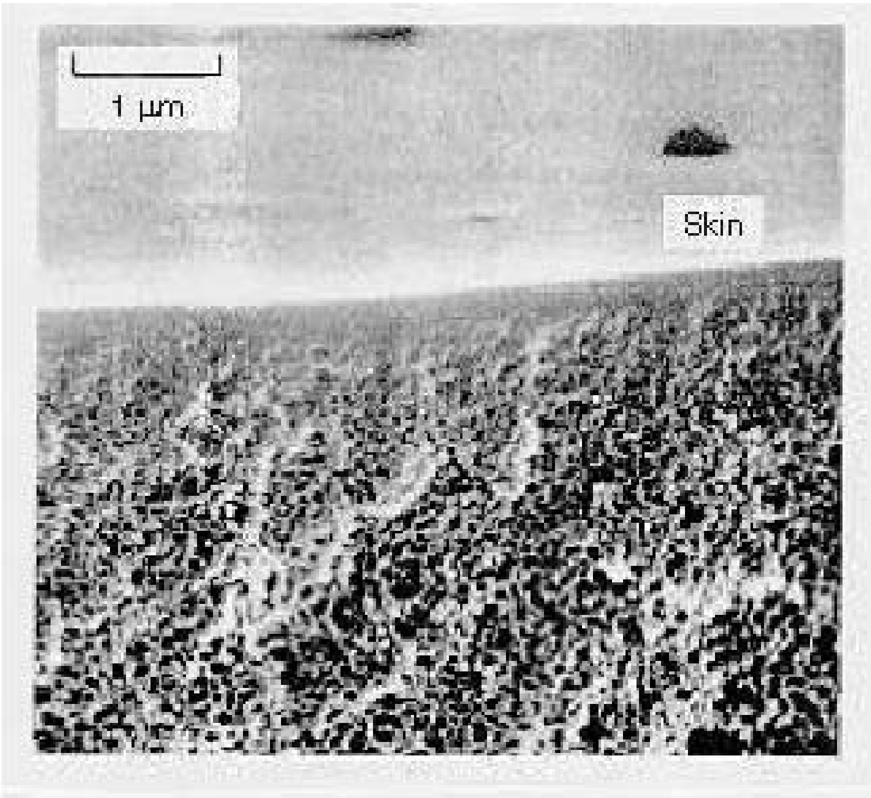

Figure 4. Asymmetric hollow-fiber morphology exhibiting a dense skin.

The desired morphology of the fiber wall frequently dictates the spinning method. The basic morphologies of membranes are: isotropic, dense or porous; and asymmetric (anisotropic) and composite types, having a tight surface (interior or exterior) extending from a highly porous wall structure (Figure 4). The tight surface can be a dense, selective skin, permitting only diffusive transport, or a porous skin, allowing viscous flow of the permeate as in conventional ultrafiltration (Figure 5) or reverse osmosis. Membrane-separation is achieved by use of these basic morphologies. The semipermeability of the porous morphology is based essentially on the spatial cross-section of the permeating species and sieving effect, i.e. small molecules exhibiting a higher permeation rate through the fiber wall. The semipermeability or anisotropic morphology of the dense membrane which exhibits a dense skin, is obtained through a solution-diffusion mechanism. The permeating species chemically interacts with the dense polymer matrix and selectively dissolves in it, resulting in diffusive mass transport along a chemical potential gradient. Thus, the dense membrane may exhibit semipermeability toward the large molecules with which it interacts, whereas the smaller, noninteracting species do not permeate. This is well demonstrated in the pervaporation process, where one-stage separation of toluene, as the permeating species, from its mixture with hexane or pentane can be accomplished employing alloys of cellulose acetate-polyphosphonate for the hollow-fibers (Cabasso and Leon 1975).

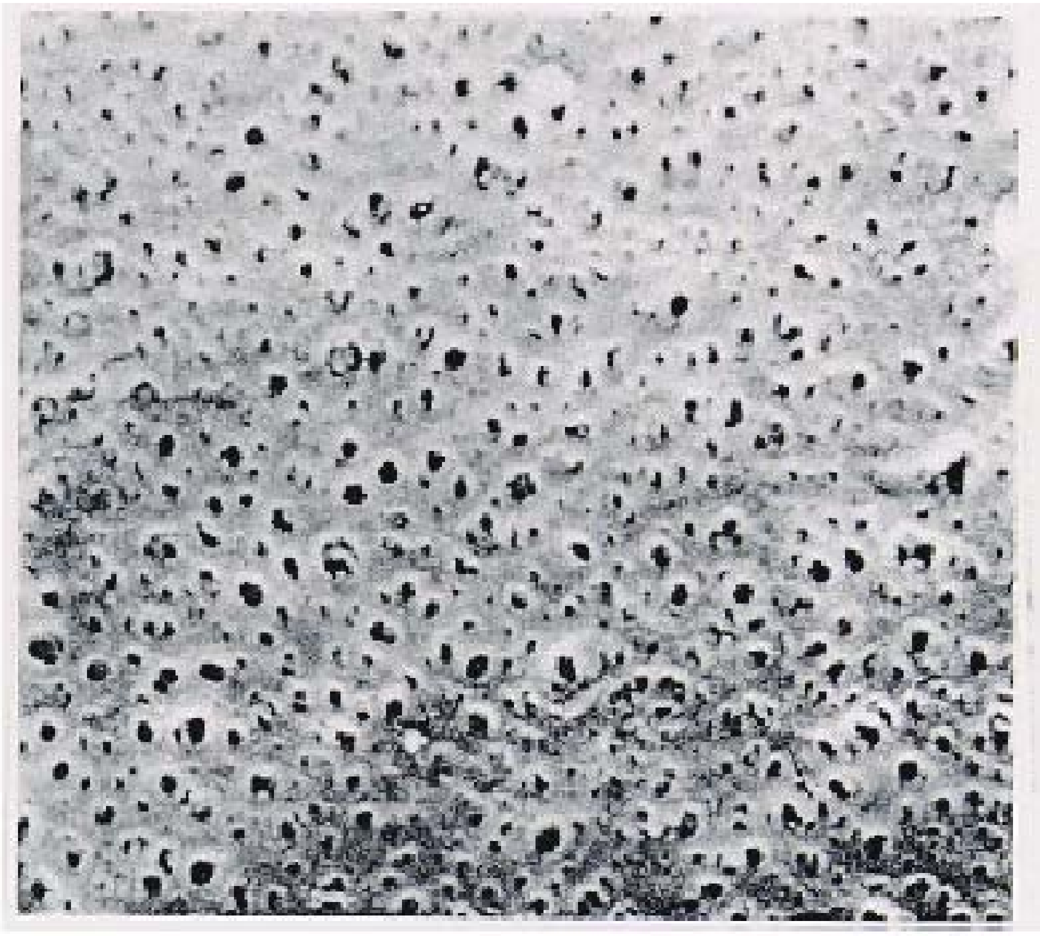

Figure 5. Surface of a polysulfone ultrafiltration hollow-fiber membrane spun with poly(vinylpyrrolidone) (3). Surface pore diameter is 0.2-0.4 μm.

The asymmetric configuration is of special value. In the early 1960s, the development of the asymmetric membranes by Loeb and Sourirajan (1962) exhibiting a dense, ultra thin skin on a porous structure provided the impetus to the progress of membrane separation technology. The rationale behind this development is that the transport rate through a dense membrane is inversely proportional to the membrane thickness, and membrane permselectivity is nearly independent of thickness. Thus, membranes with this structure can in principle permit high transport rates, yet yield excellent separation. High standards in manufacturing for reproducibility and quality control of the membranes are essential to maintain the integrity of the separation process. In addition, mechanical integrity or stability problems associated with ultra thin membranes are obviated by the use of asymmetric morphologies.

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