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Rev. Sci. Instrum. 95, 033906 (2024)
https://doi.org/10.1063/5.0176413
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ABSTRACT
Aligned with the recent trend and imperative to reduce separation layer thickness in gas separation membranes to the nanometer scale in order to raise permeance to levels that can render them competitive with respect to other gas separation technologies, a novel approach and device for fabricating defect-free composite hollow fiber (HF) membranes by dip-coating is described. The presented method avoids the fundamental drawbacks of state-of-the-art techniques for applying a thin gas separation layer onto a porous HF substrate, providing a safe but, at the same time, easily up-scalable way of producing HF membranes at a relatively high production rate. As a basic concept, hanging HF substrates are coated by allowing the coating solution to flow and drip along their external surface. The adaptability of this method, stemming from the array of available coating solutions (a plethora of dispersed nanofillers) and the multitude of substrate options, holds great promise for the fabrication of highly selective and defect-free composite HF membranes.

INTRODUCTION
The typical polymer-coating procedures in upscaled processes for composite HF membrane production usually involve a reel-to-reel system, which passes the membrane through a dip-coating solution or a spray-coating region, followed by drying and winding onto the final reel. An example of such a process from a published work is shown in Fig. 1(a). One drawback inherent in such systems is the risk of defect formation in the separation layer of the membrane (which in the case of state-of-the-art membranes for gas separation applications is ultrathin, often on the nanometer scale) since mechanical stresses/strains are imposed on it as the hollow fiber undergoes bending over reels inside and/or immediately after the dip-coating bath. The same problem of reels damaging the very thin polymeric separation layer also arises in the case of one-step composite HF fabrication with a double spinneret, i.e., where the separation layer is co-extruded by a dual-layer extrusion process, as illustrated in Fig. 1(b). In this process, the substrate polymer and separation layer polymer solutions are simultaneously fed to an inner and an outer spinneret channel, respectively. As is the case in any wet-spinning setup, the produced composite hollow fiber comes into contact and is bent over guiding wheels and a pulling wheel, yet the extruded ultrathin separation layer, which is at the hollow fiber exterior, may undergo potentially damaging stresses. A further disadvantage of this approach is that only spinnable separation layer solutions can be used. This constraint is frequently met, depending on the specific polymer–solvent–non-solvent system in use; e.g., in the case of coating with water-soluble polymers, water cannot be used as a coagulant.

Slower, but yet less “risky,” systems for HF coating involve the coating process downstream of HF cutting since, by adopting this approach, the possible detrimental effects of reels exerting pressure on the sensitive separation layer are avoided. Among these alternative methods, the simplest is depicted in Fig. 1(c), wherein a hanging
HF with sealed ends is subjected to dip-coating. However, this technique introduces an additional step of HF end sealing and also involves the peculiarity of the exertion of a buoyant force on the HF during immersion, which is caused by trapped air within the HF bore and can significantly deform the swelled HF by bending, especially in the case of longer fibers. A slight modification/refinement of this method is presented in Fig. 1(d), where the HF bending is avoided by using an HF-holder/scaffold on which the HF is mounted during the dip-coating process. In this latter case, mounting the HF is one additional step, while HF end sealing must still be applied.

In a different approach, illustrated in Fig. 1(e), the bending problem is circumvented by applying the selective layer to the internal HF wall while pumping the coating solution through the HF’s bore. Nonetheless, pressure buildup restricts HF length and introduces the need for additional equipment, such as a syringe pump, and difficulties regarding sealed tube-adjustments to HF ends are among the basic complications of this method. Finally, the wet impregnation technique [Fig. 1(f)], which places the coating step after membrane potting, is an easily applicable approach, where the coating solution is pumped through (or is simply filling) one side of the membrane module while vacuum suction is applied to the other side of the membrane. In this case, the risk of separation layer deterioration from curing-initiated heating during potting is avoided. Nevertheless, incomplete coverage and the tendency of HFs to stick together via the applied coating, especially when packing density is high, are problems often arising in this case, with each failure resulting in an entire module being lost or in a reduction of the total active membrane area. Additionally, the use of vacuum force is energy consuming, and a portion of the coating material is lost during the process as it is also deposited at the module’s walls, even if the coating solution is fed from the bore side, compounding the inefficiencies of the technique.

In this work, an innovative dip-coating method and device for the preparation of defect-free composite HF membranes are presented. The proposed method offers a range of significant advantages, such as (i) treated and coated HFs remain untouched by reels or other mechanical parts, mitigating potential contact-related issues, (ii) risks arising in wet impregnation methods are circumvented and the requirement for energy-intensive vacuum application is eliminated, (iii) remarkably, the amount of required coating solution is significantly reduced compared with conventional dip-coating and HF bending is also averted even with extended hollow fibers, (iv) possibility of achieving rapid coating times, when the coating head speed is elevated, and (v) the flow of the coating solution functions as a cleaning agent for the HF’s surface. This is of high importance because the lack of substrate cleaning could lead to the accumulation of small particles and debris on the surface, resulting in its contamination and potentially causing defects within the coating layer. Overall, in Fig. 2, the flowchart illustrates the different phases involved in the production of hollow fiber membranes, while this depiction includes the coating techniques presented in Fig. 1 alongside the proposed method.

**DESCRIPTION OF THE COATING DEVICE SETUP AND ITS FUNCTION**

As depicted in Fig. 3, the coating setup includes a support stand (designated as 8), which holds the hanging HF (2) and the movable...
coating head (5), so this arrangement ensures that the HF is kept still and straight, passing along a vertical symmetry axis through a central aperture in the coating head, while the latter can move up and down in the vertical direction without contacting the HF. The upright component of the stand is an aluminum profile with a rail to which a timing belt is affixed. A DC motor (4) (or stepper motor) is mounted on one side of a movable gantry (7), while on its opposite side, the coating head (5) is also mounted on it. A timing pulley connects the shaft of the DC motor with the timing belt so that the gantry (along with the coating head) can move in a vertical direction along the rail of the support stand. A 6-pin toggle switch (9) establishes a link between a power supply (10) and the DC motor so that the gantry can move either upward, downward, or stand still. Two pegs (6) are attached to the HF’s two ends, where one peg serves as a mounting terminal that can adhere to a magnet (11) on the stand and the other as a hanging/suspended weight that keeps the HF straight in a vertical position.

In addition, as shown in Fig. 4, coating head (5) consists of two distinct and separatable parts A and B, where part B perfectly nests inside part A in a way that allows it to be rotated within a plane vertical to the horizontal plane of the HF so that two vertical slots—one on each part—can form a zero (referred to as the “open” position for initial HF placement) or non-zero (“closed” position for locking the HF to get ready for the coating process) degree angle. At its base, the funnel-shaped coating head has a central vertical opening that surrounds the HF, and at its top, a tangential inlet tube (connected to part B) where solution (1) flows in so that it exits from the central opening in a way that forms a vortex. As the solution exits the coating head from the vertical opening, it comes into contact with the HF and flows downward along its outer surface until it drips from the lower end of the hanging HF to get collected in a beaker/receptacle. A peristaltic pump (3) circulates the solution from the collection beaker back to the head in a closed loop. During the coating process, the coating head can either remain stationary at the uppermost point of the designated “scan range” or it can move up and down, effectively “scanning” the HF. Moving the head up and down along the HF is particularly advantageous in ensuring that the entire outer HF surface becomes adequately wetted. Table I outlines the specific characteristics of the equipment utilized in the HF coating device.

With the same coating solution, numerous hanging HFs can be coated one after the other. However, the device can follow an operational cycle, which comprises multiple coatings of different, or the same, HFs using different coating solutions sequentially. In that case, prior to changing the coating solution (e.g., from an initial polymer solution with organic solvent to a subsequent aqueous polymer solution), a tube-cleaning step without hanging any HF is needed. Circulating pure solvent and/or water/alcohol/acetone through the coating head (5) so that the HF is kept still and straight, passing along a vertical symmetry axis through a central aperture in the coating head, while the latter can move up and down in the vertical direction without contacting the HF.

**TABLE I. Equipment of the HF coating device.**

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>DC motor</td>
<td>OEM JGB37-3530-178 178 RPM 12V standard gearmotor HQ</td>
</tr>
<tr>
<td>Peristaltic pump</td>
<td>Masterflex peristaltic cartridge pump of Cole Palmer (model 7519-00, L/S 7519-</td>
</tr>
<tr>
<td></td>
<td>70 cartridge) with Masterflex Tygon Lab E-3603 tubing (L/S 16, ID: 3.1 mm, hose barb size: 0.12&quot;)</td>
</tr>
</tbody>
</table>
peristaltic pump from one beaker to another, followed by blowing air through the tubing (notably, the peristaltic pump’s cartridge has to be unmounted during this step). This comprehensive process effectively ensures that the subsequent coating can proceed with the new solution without contamination from the previous one. Furthermore, including dispersed filler materials, such as graphene nanoplatelets (GNPs) or carbon nanotubes (CNTs), into the coating solution makes successful coating easier. In this case, protection measures should be taken during the described cleaning procedure, such as wearing protective gloves and a high-filtration FFP3 mask.

Furthermore, a multi-HF coating system where HF coatings could proceed in parallel is depicted in Fig. 5. In this type of setup, multiple HFs are coated simultaneously by implementing only one pump, which favors energy and cost savings when upscaling. Additionally, it should be mentioned that, compared with the setups depicted in Figs. 1(e) and 1(f), the expensive and highly energy consuming vacuum pump equipment is avoided.

Finally, as an example of implementation, a porous 70 cm long polyimide/GNP HF substrate, prepared by the dry-jet wet phase inversion process in a spinning set-up, as described in a previous study, was first coated with a flow rate set at 30 ml/min for ~1 min with 1% Sylgard 184 (cross-linked PDMS) solution in hexane 3 times, followed by 2 times with 5% Pebax-1657 in a mixed solvent of ethanol/water (70:30 ratio). The applied coating layers were left to dry under ambient conditions for 30 min after each coating was performed. The resultant thin film composite HF membrane was cut into six pieces of the same length and potted with epoxy resin (Araldite 2012) in a small compact module with an 8 cm active HF length or, equivalently, an active area of 15 cm². This example demonstrates the feasibility of the proposed method for preparing thin film composite HF membranes. In Tables I and II, the equipment used in the coating device and the HF coating parameters are summarized.

**EXPERIMENTAL PROCEDURE FOR METHOD EVALUATION**

The effectiveness of the composite hollow fiber membrane preparation was evaluated by subjecting it to gas separation testing under continuous flow conditions of a binary CO₂/CH₄ gas mixture. The permeance values for CO₂ and CH₄ through the developed HF membranes, along with the real separation selectivity of the gas mixture, were gauged based on the feed pressure. The complete measurement procedure is detailed in a previous study, and a membrane testing rig, described in detail in a previous study, was employed for this purpose. In brief, helium was employed as the sweeping gas to flush the permeate side of the membrane at a flow rate of 30 ml/min, and the feed composition for CO₂/CH₄ was 10/90 vol. %. During measurements, the permeate-to-feed flow rate ratio (determined as stage-cut) was retained under 1% to avoid concentration polarization. Gas compositions in the permeate stream were determined using an SRI 8610C gas chromatograph featuring a fused silica capillary column and a TCD detector for CO₂, as well as an FID detector for CH₄.

The gas separation factor was calculated from the subsequent equation

\[
S = \frac{(y_1/y_2)_{\text{permeate}}}{(y_1/y_2)_{\text{feed}}},
\]

**TABLE III. Gas separation performance of fabricated composite HF membrane for 10% v/v CO₂ in CH₄ [1.3 bar(a), 298 K].**

<table>
<thead>
<tr>
<th>(S) (CO₂/CH₄)</th>
<th>(P_\text{f}/P_\text{c}) CO₂ (GPU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>91.9 ± 4.3</td>
<td>0.7 ± 0.02</td>
</tr>
</tbody>
</table>

**TABLE II. Coating parameters for thin film composite HF membranes preparation.**

<table>
<thead>
<tr>
<th>Speed of coating head (m/min)</th>
<th>Flow rate of coating solution (ml/min)</th>
<th>Full HF length (cm)</th>
<th>Coating length (cm)</th>
<th>Coating scan route</th>
<th>Number of coatings</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3</td>
<td>30</td>
<td>70</td>
<td>55</td>
<td>3 times (“from lower end to higher end and back”)</td>
<td>3 (sylgard) + 2 (pebax)</td>
</tr>
</tbody>
</table>
FIG. 6. Robeson plot of CO$_2$/CH$_4$ selectivity vs membrane permeability. Comparison of fabricated composite HF membrane (red open circle) with various other polymeric membranes$^{12}$ (black filled and open circles) [Baker and Lokhandwala, Ind. Eng. Chem. Res., 47(7), 2109 (2008); Copyright 2015 Author(s), licensed under a Creative Commons Attribution 4.0 License].

where $y_i$ is the gas concentration expressed as % v/v and indices $i = 1$ or 2 correspond to CO$_2$ and CH$_4$, respectively. In addition, the permeance of each gas was calculated using the following equation:

$$(P_{ei}/l)_i = \frac{y_i \times Q}{A \times \Delta P_i},$$

where $P_{ei}/l$ is the gas permeance (in GPU, GPU = $10^{-6}$ cm$^3$(STP)/cm$^2$.s.cmHg), $Q$ is the flow rate of the membrane permeate, $y_i$ is the concentration of gas $i$ in the permeate stream, $A$ is the surface area of the membrane (15 cm$^2$, as aforementioned), and $\Delta P_i$ is the partial pressure drop across the membrane for gas $i$.

The composite HF membranes were modulated and hermetically sealed using epoxy resin within a custom stainless-steel module designed to accommodate 6 hollow fibers, each measuring 8 cm in effective length. Afterward, each module was allowed to cure for a duration of 24 h at room temperature prior to assessment. The experiments were conducted with feed gas flows on the shell side, and the membrane module was tested under feed pressures of up to 6 bar. Moreover, pressurization-depressurization cycling was utilized to explore the stability and potential reversibility of structural changes in the membranes caused by pressure application. The obtained outcomes are depicted in Table III, revealing that this innovative method and device for coating composite HF membranes, ensuring enhanced efficiency, minimized risks, and elevated membrane quality. The viability of this approach was explored through the assessment of the produced thin-film composite HF membranes with a real binary CO$_2$/CH$_4$ mixture (10/90 vol. %) under continuous flow and elevated pressure conditions. The successfully fabricated membranes exhibited commendable performance, indicating the potential promise of this method for preparing composite membranes and establishing the feasibility of a straightforward and smooth scale-up of the process.

These encouraging initial findings pave the way for a straightforward scale-up of the process, presenting the potential to produce highly selective composite membranes on a larger scale. Furthermore, this method can seamlessly integrate into the membranes’ production process.

CONCLUSION

In this study, the limitations of conventional methods for coating HF membranes were emphasized. An innovative device/strategy is introduced with the aim of addressing these issues and presenting the advantages linked to this novel approach. The detailed description of the setup and procedure provides a promising alternative for coating composite HF membranes, ensuring enhanced efficiency, minimized risks, and elevated membrane quality. The viability of this approach was explored through the assessment of the produced thin-film composite HF membranes with a real binary CO$_2$/CH$_4$ mixture (10/90 vol. %) under continuous flow and elevated pressure conditions. The successfully fabricated membranes exhibited commendable performance, indicating the potential promise of this method for preparing composite membranes and establishing the feasibility of a straightforward and smooth scale-up of the process.

ACKNOWLEDGMENTS

The projects (1) “GG-CO$_2$” (T2DGE-0183), co-funded by Greece and the European Union through the European Regional
Development Fund, and (2) "GRAPHITE" (MIS 5185058), co-funded by Greece and the European Union through the framework program ATTIKI 2014–2020, are acknowledged.

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Dionyssos S. Karousos: Conceptualization (equal); Data curation (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Supervision (equal); Validation (equal); Writing – original draft (equal); Writing – review & editing (equal). Francesco Chiesa: Investigation (equal); Methodology (equal). George V. Theodorakopoulos: Conceptualization (equal); Data curation (equal); Methodology (equal); Supervision (equal); Validation (equal); Writing – original draft (equal); Writing – review & editing (equal). Mirtat Bouroushian: Supervision (equal); Validation (equal); Writing – review & editing (equal). Evangelos P. Favvas: Conceptualization (equal); Funding acquisition (equal); Project administration (equal); Resources (equal); Supervision (equal); Validation (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES