PERSPECTIVE ON 3D PRINTING OF SEPARATION MEMBRANES AND COMPARISON TO RELATED UNCONVENTIONAL FABRICATION TECHNIQUES

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ABSTRACT

Additive manufacturing, likewise known as 3-dimensional (3D) printing and rapid prototyping, has the ability to create almost any geometrically complex shape or feature in a range of materials across different scales. It has found its applications in various areas, such as medicine (bioprinting), art, manufacturing and engineering. On the other hand, its use in separation membrane engineering is relatively new. The use of additive manufacturing techniques could provide more control towards the design of separation membrane systems and offers novel membrane preparation techniques that are able to produce membranes of different shapes, types and designs which cannot be made using conventional techniques such as phase inversion or sintering. Here we provide key background information on 3D printing technologies and applications in membrane engineering; a discussion of the potential and limitations of current 3D printing technologies for membrane engineering and future aspects of the technology. Due to the potential benefits of 3D printing in membrane manufacturing, in particular the unprecedented control over membrane architecture the technique could allow, the use of 3D printing in membrane systems should see significant growth in the near future.

Keywords: 3D printing, additive manufacturing, subtractive manufacturing, membrane, separation, rapid prototyping
1. INTRODUCTION

The invention of the first printing press around the 1440s facilitated rapid reproduction of text and images and dissemination of information.[1] Current printed materials are produced using modern offset printing, which involves employing inks made up of light-sensitive chemicals to transfer text and images to printing papers. Over the past few decades, printing technology has advanced from two-dimensional (2D) printing to three-dimensional (3D) printing in which 3D shapes are created by successive deposition of layers of materials.[2] 3D printing, more commonly referred to as additive manufacturing (AM) in the late 20th century, creates end-use products bottom-up, by depositing one layer of material at a time.[3] It has the ability to create almost any geometrically complex shape or feature in a range of materials across different scales.[4] The introduction of AM has revolutionized the prototyping and manufacturing industry, which previously relied on more expensive and time consuming methods such as moulding, forming and machining. Due to its extensive application in making prototypes, the term rapid prototyping (RP), which describes the use of the technology, is also often used to describe the technique. Another term– 3D printing (3DP) was later introduced and was originally referred to the technique that use a inkjet printing head to sequentially deposit 2D material layer-by-layer onto a powder bed to form a 3D structure.[5] While AM may be a more general term suitable to describe the technique, 3DP has gained popularity over time and has now expanded to encompass a wider variety of techniques including, stereolithography (SLA), sintering[6] and extrusion-based processes.[7] All three terms (AM, RP, and 3DP) are still used in the literature, but may or may not refer to the overarching AM technique. AM begins with a 3D model (or computer-aided design (CAD) drawing), which is sliced into layers and printed layer-by-layer into a 3D build.[8] Materials that can be printed now include conventional thermoplastics, ceramics, metals and graphene-based materials.[9] AM is driving major innovation in many areas including in medical,[1, 4] art,[10] education,[11, 12] manufacturing and engineering.[13, 14] Very recently, the use of AM have been extended to membrane systems, including spacers and membranes.[15-17] The use of AM in separation membrane printing is an exciting new area of research. The past 10 years has seen great advances in AM technology allowing greater control, resolution and precision that is finally allowing separation membranes to be fabricated by this increasingly important and flexible manufacturing technique. AM offers a different membrane fabrication method which complements conventional techniques such as the phase inversion method (non-solvent induced and thermally induced), enabling the potential to produce membranes of different shapes, types, and designs which can be more precisely designed, fabricated and controlled than any other fabrication membrane method available currently. Additionally, almost uniquely it allows both the micro- and macro-structure of the membrane to be designed and fabricated in one go, allowing membrane module fabrication to be controlled in a single machine/process from membrane material through to membrane module, giving the unprecedented combined and integrated design possibilities for improving both the membrane separation at both the materials and process architecture levels. However, there exist several limitations of the techniques that still need to be addressed. To help unlock this exciting and vast new area, herein we revisit current available AM techniques and discuss the potential application of various AM technologies to separation membrane engineering. Readers are also referred to a recent review on AM techniques targeted for membrane spacers and membrane modules.[18] The current perspective will differ considerably from this review, as our emphasis will not be on membrane modules and spacers, all of which can in the main be achieved with current and conventional AM technologies. Instead, the emphasis of this perspective will be given to the specification of the techniques and printable materials in order to identify their suitability for separation membrane engineering. To do this we will discuss the limitations of current technologies, methods that could potentially overcome these limitations and future perspective of printing techniques for membrane engineering. This provides a new and future-focussed perspective for membranes and AM, distinct from but complementing other references.[18]
2. TECHNIQUES AND SPECIFICATIONS

Various techniques have been developed for AM and can be generally categorized into four types (Figure 1): (i) photopolymerization, (ii) powder, (iii) material extrusion, and (iv) lamination. A comparison of these techniques, including the advantages, disadvantages, printable materials and specifications, is summarized in Table 1. Among which, photopolymerization is currently the most popular method for membrane fabrication. The other three AM types are also constantly improving, but due to their limited resolution, these systems are currently not quite applicable to membrane fabrication and membrane systems. Below is a short summary of current membrane technologies to provide context to the ensuing discussion. More detailed explanations and reviews of these techniques can be found in [19, 20].
2.1 Photopolymerization

The main AM technique that can and will be used in membrane fabrication is based on photopolymerization (Figure 1), which in general refers to the curing of photo-reactive polymers (otherwise known as photopolymers) with a laser, UV or light. Amongst these, photopolymerization based on laser lithography is the most promising one for membrane fabrication. The most common laser-lithography-based technique is known as stereolithography (SLA). An ultraviolet (UV) laser is used to trace and therefore cure the model’s cross-section, while the remaining area remains in liquid form. Once the trace is completed, the platform is lowered and the part is coated with a new layer of resin. The process is repeated until the entire part is finished. The final part is then put in an UV oven to complete the curing process. Modern SLA printers have the part raised from the resin during printing (e.g. Formlabs). A similar technique, based on SLA, has also been developed, known as the direct light processing (DLP) printing. In this, instead of using a UV laser, a DLP projector is used to project the entire cross-sectional layer of the 3D structure. Likewise, printing could occur with platform going downwards or upwards, but the latter is the state of the art.

A technological breakthrough in photopolymerization was reported last year, where the print time can be reduced by 25 to 100 times. This technique, known as continuous liquid interface production (CLIP) is based on DLP. Traditional DLP techniques require the cured layer to be mechanically separated from the bottom of the vat containing the resin, followed by resin re-coating before the next layer is exposed.[21] CLIP diminishes the additional mechanical movement by forming an oxygen-containing “dead zone”, a thin uncured liquid layer at the build point which avoids adhesion to the resin vat while keeping the liquid resin in place for the next layer. This approach eliminates the separate and discrete steps required for the traditional SLA printer and radically reduces the build time between layers. The end result is super-fast 3D printing—quicker than any other of the SLA printers—while maintaining feature resolution below 100 micrometers.[21] Two other comparable patent pending techniques (NEXA3D and NewPro3D) could also achieve such printing speed, if not faster but details of their technologies are not yet available.

The highest resolution AM (of about 100 nm) is achieved using two-photon polymerization (TPP).[8, 22] Briefly, the technique is based on the simultaneous absorption of two photons, which induces photochemical or physical transformations within a transparent resin. The inherent optical nonlinearity of two-photon absorption allows localized absorption in regions of high light intensities, i.e. the reaction is restricted to occur within the vicinity of the focal spot of the laser beam, a volume as small as a few attoliters.[23]

Material jetting 3D printer (also known as inkjet 3D printer) is based on the principle of customary paper printer, but utilize light-curable resins in place of the usual inks. Two resists are used— build material and support material. The support material is subsequently removed after completion of 3D printing to reveal the printed features.

The other three AM types are also constantly improving, but due to their limited resolution, these systems are currently not quite applicable to membrane fabrication and membrane systems.

2.2 Powder

Powder-based printing systems, as the name suggests, involve the use of powder-type material for printing. General examples include binder jetting, where a chemical binder is jetted onto the spread powder to form the layer; and selective laser sintering (SLS) where a laser is used to sinter the materials such as thermoplastics, metal and ceramics. Binder jetting techniques first create the model layer-by-layer by spreading a layer of powder and printing the binder onto the powder bed with similar methods employed in conventional ink-jet printing.[4] The step is repeated until the 3D structure is obtained. The loose powder that was not hardened acts as a support for subsequent layers.
On the other hand, selective laser sintering (SLS) or direct metal laser sintering (DMLS) involves using a high power laser to sinter small particles of thermoplastic, metal, ceramic or glass powders. The main difference is that SLS uses powder rather than liquid polymer. When the laser beam hits the powder, the intense heat sinters the powders together, while the unsintered materials in each layer act as support structures. Other similar technologies such as selective laser melting (SLM) and electron beam melting (EBM) melt the metal powder instead of sintering the metal powder.

2.3 Material extrusion

In material extrusion-based printing systems, fused deposition modelling (FDM, otherwise known as fused filament fabrication, FFF) works by extruding a filament of polymeric material at the appropriate temperature.[7] The nozzle is heated to melt the thermoplastics past their glass transition temperature before depositing them layer-by-layer. The extruded hot material hardens and adheres to the preceding layer.

Another example, although often not included in AM review articles, is a method known as direct writing assembly (DWA) which refers to fabrication methods that employ a computer-controlled translation stage, such as a material deposition nozzle, to deliver a filament of viscoelastic material and create objects with controlled architecture.[24] More details about DWA are available in reference [24, 25].

The 3D bioplotter is another extrusion-based printer which disperses viscous plotting material into a liquid medium with a matching density.[26] The technique is capable of extruding a wide variety of materials, including pastes, solution and dispersions of polymers and blends.[27] Most interestingly, materials such as hydrogels[28] and aqueous biosystems (cells)[29, 30] can also be engineered into the scaffold.

2.4 Lamination

In lamination-based prototyping, laminated object manufacturing (LOM) works by layering sheet materials which are cut and laminated together to form a prototype. First, the feeder/collector mechanism advances the sheet over the build platform. Next, a heated roller applies pressure to bond the sheet to the base or the previous layer. On one side of the layer is an adhesive coating for bonding. The laser traces the outline and crosshatches the excess area for waste removal. The platform is then lowered and a new sheet of material is feed for the next layer. This process is repeated as needed to finish the part.

Another laminating-based system, known as selective deposition lamination (SDL), uses paper as its only building material and is capable of printing in more than one million colours. Before printing, stacks of standard papers, each pre-colour-printed with a cross-sectional cut of the final prototype, is loaded into the feeding tray. The SDL process is as follows: Adhesive is selectively applied to the first sheet of paper. Instead of gluing the whole layer (as is done in LOM), SDL deposits higher a density of adhesive in the area that will become the prototype, and a lower density of adhesive in the surrounding area of the prototype layer that will function as support. A new sheet of paper is fed from the paper feed mechanism on top of the freshly applied adhesive. The build plate is shifted up to a heating plate and pressure is applied. After the build plate returns to its initial position, an adjustable blade traces the prototype outline to create the edges of the part. The process is repeated until completion of the work. SDL cannot be directly used for 3D printing of membranes due to the intrinsic lack of resolution and material, but its working concept can be adopted for membrane design.
| Technique       | Resolution | Maximum build-space (mm) | Accuracy (µm) | Printing speed | Material               | Advantages                                                                 | Disadvantages                                                                 | Company                                                                 |
|-----------------|------------|--------------------------|---------------|----------------|------------------------|-----------------------------------------------------------------------------|------------------------------------------------------------------------------|--------------------------------------------------------------------------|
| Photopolymerization |            |                          |               |                |                        |                                                                             |                                                                              |                                                                          |
| SLA             |            |                          |               |                |                        |                                                                             |                                                                              |                                                                          |
| 3D Systems:     | 50 µm (1.27 | 1500 × 750 × 550         | 25–50 per     | N/A            | Photopolymers          | ◦ Capable of printing complex geometry ◦ Good accuracy                      | ◦ Require support structures ◦ Hazardous resins ◦ Limited to curable materials ◦ Slow | 3D Systems, USA; Old Word Labs, USA; CMET, Japan; D-MEC, Japan; Abee, Japan; Lithoz, Austria; DWS, Italy; 3DCeram, France; XJRP, China; Wuhan Binhu, China; Union 3D, China |
|                 | µm; by laser |                          | 25400         |                |                        |                                                                             |                                                                              |                                                                          |
| 3D Systems:     | 15–100 µm  |                          | N/A           | 10 mm/h        | Photopolymers          | (Compared to SLA technology) ◦ Higher speed and resolution ◦ No beam acceleration or deceleration ◦ Less distortion | Same as SLA                                                                  | EnvisionTEC GmbH, Germany                                                                 |
|                 |            |                          |               |                |                        |                                                                             |                                                                              |                                                                          |
| DLP             | 15–150 µm  | 192 × 120 × 230          | N/A           | N/A            | Photopolymers          | ◦ Faster than SLA                                                          | Same as SLA                                                                 | EnvisionTEC GmbH, Germany; Prodways, France; Rapidshape, Germany                                                                 |
|                 |            |                          |               |                |                        |                                                                             |                                                                              |                                                                          |
| Material        |            |                          |               |                | General: Photopolymers, Optomec: Photopolymers, metal, carbon, ruthenate, SWCNT, MWCNT, PEDOT: PSS, polyimide, PVP, general solvents, acids & bases, DNA, Proteins, Enzymes | Short build time ◦ high resolution ◦ Parts can be printed in range of colours | Limited mechanical properties ◦ Relatively poor surface finish ◦ Newly printed parts require post-processing | 3D Systems, USA; Stratasys Inc., USA; Optomec, USA                                                                       |
| jetting         |            |                          |               |                |                        |                                                                             |                                                                              |                                                                          |
| 3D systems:     |            |                          |               |                |                        |                                                                             |                                                                              |                                                                          |
| 600 × 540 dpi   | 508 × 381 × | 517.78 × 380.75 × 294.39 | 25–40 per     | N/A            |                        |                                                                             |                                                                              |                                                                          |
|                 | 299 (colour |                          | 500           |                |                        |                                                                             |                                                                              |                                                                          |
|                 | printing); |                          | 200 (colour    |                |                        |                                                                             |                                                                              |                                                                          |
|                 | 380 dpi    |                          | printing)     |                |                        |                                                                             |                                                                              |                                                                          |
|                 | 300 dpi    |                          | 300 (colour    |                |                        |                                                                             |                                                                              |                                                                          |
| Stratasys:      | X/Y: 600 dpi|                          | 1000 × 800 × 500 |                |                        |                                                                             |                                                                              |                                                                          |
|                 | Z: 1600 dpi |                          |               |                |                        |                                                                             |                                                                              |                                                                          |
|                 | X/Y: 300 dpi|                          |               |                |                        |                                                                             |                                                                              |                                                                          |
|                 | Z: 1600 dpi |                          |               |                |                        |                                                                             |                                                                              |                                                                          |
| CLIP            | 50 µm      | 144 × 81 × 330           | N/A           | N/A            | Photopolymers          | ◦ Very fast printing ◦ Layerless                                            | Small build size                                                            | Carbon3D, USA                                                              |
|                 |            |                          |               |                |                        |                                                                             |                                                                              |                                                                          |
| TPP          | 0.15 μm | 100 × 100 × 3 | N/A | 100 μm/s | Photoresists (IP-L, IP-G, SU-8, chalcogenide glass, ormocere, PEG-DA etc.) | Nanometer resolution | Small build size | Expensive | Slow printing speed | Require materials of high optical transparency | Nanoscribe GmbH, Germany |
|--------------|---------|---------------|-----|----------|--------------------------------------------------------------------------------|----------------------|-----------------|----------|-------------------|-----------------------------------------------|--------------------------|

### Powder

| Binder jetting (Digital Sand Casting) | Voxeljet: 200–600 dpi ExOne: X/Y: 0.0635–100 μm Z: 1 μm | Voxeljet: 4000 × 2000 × 1000 ExOne: 2200 × 1200 × 700 | N/A | Voxeljet: 12–36 mm/h ExOne: 20–400 L/h | Polymer, metals, alloys and ceramics | Short build time | Cheap | Does not employ heat | Parts can be printed in range of colors | Limited mechanical properties | Additional post processing can add significant time to the overall process | Not always suitable for structural parts | ExOne, Germany; Voxeljet, Germany |

| SLS/ DMLS | 3D systems: 80–150 μm EOS: Plastic: 60–180 μm Metal: 30–500 μm | 3D systems: 550 × 550 × 750 EOS plastic: 700 × 380 × 560 EOS metals: 400 × 400 × 400 | N/A | 3D systems: 0.9–5 L/h EOS plastic: 7–48 mm/h EOS metal: N/A | Thermoplastics, metal powders, ceramic powders | No need post-curing (except for ceramic) | Do not require support structures | Porous surface | Poor surface finishes | May require long heating and cooling time | 3D Systems, USA; EOS GmbH, Munich, Germany; Matsura, Japan; XJRP, China; Wuhan Huake 3D, China; Wuhan Binhu, China; Trump Precision Machinery, China; Long Yuan AFS, China |

| SLM/ EBM/ DMP | 3D systems: 10–50 μm SLM: 20–200 μm Renishaw: 20–100 μm | 3D systems: 500 × 500 × 500 SLM: 500 × 280 × 325 Renishaw: 245 × 245 × 300 | N/A | 3D systems: 55–80 cm³/h SLM: 20–105 cm³/h Renishaw: 5–20 cm³/h | Titanium alloys, cobalt chrome alloys, nickel-base alloys, tool steels, stainless steel, aluminium etc. | Vast range of materials | Availability of desktop scale printer | Require support structures | Reduced strength in the vertical direction | Grainy appearance | Slower than laser or print head but overall | 3D Systems, USA; SLM Solutions GmbH, Germany; Renishaw, UK; Wuhan Binhu, China; Arburg, USA; CLAD, France; Optomec, USA; Concept Laser, Germany; Realizer, Germany; Arcam, Sweden; Sisma, Italy |

### Material extrusion

| FDM/ FFF | Stratasys: 127–330 μm | Stratasys: 914 × 610 × 914 | Stratasys: 1.5–89 | N/A | Thermoplastics, modeling clay, plasticine, metal clay, eutectic metals | Vast range of materials | Availability of desktop scale printer | Require support structures | Reduced strength in the vertical direction | Grainy appearance | Slower than laser or print head but overall | Stratasys Inc., USA; Cosine Additive, USA; Cincinnati, USA; Scicaky Inc., USA; DMG Mori, USA; MASSIVit 3D, Israel; Mutoh |
| Process Type | Acronyms | Material Properties | Process Speed | Company/Origin |
|--------------|----------|---------------------|---------------|----------------|
| **3D Bioprinting** [31, 32] | EnvisionTEC: 100 µm | EnvisionTEC: 150 × 150 × 140 | EnvisionTEC: 1 | EnvisionTEC: 0.1–150 mm/s | + Vast range of materials including biocompatible and medical-grade materials | + Small build size | + Time consuming technique due to requirement of optimization of the plotting conditions for each different material | EnvisionTEC GmbH, Germany; BigRep GmbH, Germany; GeSiM, Germany; Organovo, USA; Cyfuse, Japan; Regenova, Japan; |
| **LOM** | Z: 100 µm (paper); 150 µm (plastic) | N/A | N/A | Paper, metal foil, plastic film | + Fast build | + Relatively cheap | + Poor strength | + Wooden parts may absorb moisture | + Newly printed parts require post-processing | Cubic Technologies, USA |
| **SDL** | X/Y: 12 µm; Z: 100 µm | 256 × 169 × 150 | N/A | Paper | + Full colour printing | + Low cost print material | + Eco-friendly | + Only capable of printing standard paper | + Parts may absorb moisture | + Obvious stairstepping on edges of parts | Mcor Technologies, Ireland |

* Note: Specifications as obtained from manufacturers’ website. Test methods may vary among manufacturers. Resolution is geometry dependent. Accuracy is material dependent. Printing speed does not consider additional steps (such as post-processing, handling etc.). Acronyms: stereolithography (SLA), Scan, spin and selectively photocure (3SP), direct light processing (DLP), continuous liquid interface production (CLIP), two-photon polymerization (TPP), selective laser sintering (SLS), direct metal laser sintering (DMLS), selective laser melting (SLM), electron beam melting (EBM), direct metal printing (DMP), fused deposition modelling (FDM), fused filament fabrication (FFF), laminated object manufacturing (LOM), and selective deposition lamination (SDL).

1. http:// envisiontec.com/company/3d-printer-technologies/
2. http://www.optomec.com/additive-manufacturing/printed-electronics/aerosol-jet-materials/
3. SCREENING OF AM TECHNIQUES FOR MEMBRANE FABRICATION

Different AM techniques have their unique advantages and disadvantages which make them more suited for particular applications over the others. To determine the suitability of the AM techniques for membrane fabrication, several key properties of the techniques need to be considered (Figure 2). This screening is unique to this study since the methods were screened for membrane fabrication rather than for membrane spacers and modules (as per [18]) due to the higher demand in AM capability required for printing membranes.

![Figure 2. Key properties of 3D printing techniques.](image)

For membrane fabrication, the following characteristics are desired:

- **Resolution**: High resolution needed – in nanometer range resolution
- **Accuracy**: Need to be able to print the membrane as designed, inclusive of the effect of pre-treatment and post-treatment steps (e.g. removal of support material)
- **Build size**: Need to be able to print actual membrane sizes (e.g. >1 metre in width)
- **Speed**: Generally as fast as possible to minimise build time
- **Printed materials**: Extension of compatible 3D printable materials to include the common materials used for membranes
- **Mechanical properties**: Materials which are able to resist high pressure processes (1–40 bar) and a range of different solutes and solvents
- **Support**: Smooth (low roughness) and strong support that can be easily removed or AM system that does not need support
- **Cost**: Competitive and comparable to phase inversion membrane fabrication.

The capabilities of the current AMs as well as the advantages and disadvantages in these areas are considered below. Comparable characteristics of the AMs are grouped and discussed together to provide a clearer overview of the available AM techniques and their potential for membrane design. These are then used as benchmarks against which to understand what has been done (and why; Section 4) and the future potential of AM if we can overcome any limitations in the current AM capabilities (Section 5).
3.1 Resolution, accuracy, build size and speed
Among the current available techniques, the TPP technique can produce prototypes with a resolution below 100 nm due to its localized small polymerization volume.[33] The Photonic Professional GT (Nanoscribe, Germany), a TPP-based 3D printer, has a 3D lateral feature size of less than 200 nm (2D lateral resolution of 300 nm and vertical resolution of 800 nm). It has an accessible writing area of 100 × 100 mm² and writing speed of 0.1 to 10 mm/s. As printing requirement reaches the theoretical resolution of the printer, the printing time generally increases rapidly and printing fine features of the desired 3D model may become challenging i.e. the printer could not print the model exactly as designed. Nevertheless, the printer resolution can be improved with the improvement over the technology or laser source. Very recently, a 1.5 Ångström wavelength laser has been designed,[34] The adaptation of new laser sources in the near future could substantially improve the resolution of AM printer.

Very recently, a new SLA-based printer was introduced by Old World Labs, USA. The new model, MC-2 purportedly has a resolution of 100 nm (material dependent), accuracy of ±50 nm and build volume of 152 × 152 × 152 mm³. The printer can print a volume of ~16500 mm³ in an hour (resolution dependent). By comparison, a SLA printer (e.g. Projet 7000 HD, 3D systems, USA) has a highest resolution of 50 µm, accuracy of 0.025 to 0.050 mm per 25.4 µm of part dimension and a much larger build volume of 380 × 380 × 250 mm³. The multi-jet printer based on material jetting (e.g. Projet 3500 HDMax, 3D Systems) from the same company on the other hand can produce material with a resolution of 16 µm in a build volume of 298 × 185 × 203 mm with similar accuracy. In terms of resolution and accuracy, the material jetting printer of Stratasys performs similarly.

A FDM-based printer, such as the Stratasys Fortus 900mc, has a layer thickness of 178 µm, accuracy between 8.9 to 37.1 µm per µm and a huge build volume of 915 × 610 × 915 mm³. FDM has limited application to printing membranes now and perhaps in the future since the highest resolutions of FDM-based printers are limited by the technique. The resolution, like 2D printers, is dependent on the droplet generation technique, nozzle size, printing material property and substrate property. The resolution of material jetting printer is also limited by the same, but unlike FDM, higher resolution can potentially be achieved by modifying substrate wettability so the spreading can be controlled.[35] In general, engineering a hydrophobic surface and low surface energy would reduce the tendency to spread, thus reducing the droplet diameter.[36-40] Therefore, the resolution can potentially be improved by successively engineering the surface of each layer as it is deposited. The formulation of the printing material will not only influence the ejecting process, but also govern the resolution of the printed patterns. Approaches such as increasing ink viscosity could limit ink spreading on surfaces (such as utilizing the so-called coffee-ring effect).[41] Apart from that, the design of printing apparatus can also improve the resolution. For instance, electro-hydrodynamic jet printing has been applied to fabricate patterns with sub-micron resolution.[42] The technique applies electric fields to generate the fluid flows for ejecting and depositing inks onto a substrate. Other techniques that can also improve the resolution are jet focusing by hydrodynamic means[43] and pyro-electrohydrodynamic shooting.[44]

Based on the above, for making membranes, in terms of resolution, accuracy, build size and speed, there are several challenges that current machines need to further develop beyond to make AM membranes feasible:

Limited resolution
The resolution is a consequence of several machine-specific parameters such as working principle of the AM, print material properties and product geometry. Therefore, the actual resolution of the product is usually lower than the nominal resolution of a 3D printer. Resolution giving feature sizes (e.g. pores) of 10 nm or smaller is needed to produce membranes for applications such as ultrafiltration, nanofiltration, reverse osmosis and forward osmosis. Despite the ‘low’ resolution, AM is still able to precisely control the production of complex structures, however this is currently capped at a resolution of ~100 nm (TPP-based AM). Future AM technologies no doubt with be produced with a finer resolution capable of building over a larger volume. Until this time, current AM can still be used in compromised solution: printed membranes with insufficient feature sizes for the desired separation can be post-modified to achieve the desired pore sizes – providing a way of producing porous features
inside designed larger membrane structures, the best that can be done until AM capability matches membraneologists’ ambitions. This is further discussed in Section 5.3.

In terms of the desired characteristics for membrane fabrication (above), most current AM systems cannot give submicron range resolution and those that do have either limited build size or are slow and expensive. Porous membranes have not yet been printed, so the accuracy of these systems in printing the membranes as designed has not yet been evaluated. In current AM technologies, bigger build size is coupled with lower resolution and vice versa. This is something that needs to be addressed in future AM system developments if membranes are to be practically fabricated.

**Poor scalability**
The scalability of AM for membrane can be difficult and costly due to complex machinery. To print a large sheet of membrane with pore size in the sub-micron scale, extensive amounts of time to produce the membrane are required. An intuitive solution is to design an AM machine with multiple laser sources/ print head/ nozzle to simultaneously print the membranes to improve speed, while retaining the printing resolution but this means much higher capital and operating cost. A possible solution may arise from layerless additive manufacturing technologies such as CLIP approach, which have substantially decreased printing time.[21]

**Rough surfaces**
Some AM techniques such as the powder-based techniques (binder jetting) may produce rough surfaces. Rough surfaces can be desirable or undesirable in membrane separations, depending on its effect on fouling behaviour and its tailorability. For example, membrane surfaces have been intentionally roughened on the nanoscale to improve anti-fouling properties.[45, 46] The roughness caused by powder-based techniques is an inherent property of the technique and so this may be beneficial in such applications.

**High computational load**
This is associated with resolution, accuracy and build size. The design of the complex membrane structure of a large membrane sheet would require tremendous computational load due to the sheer number of arrays (repeating unit). Not only is a high performance computer needed, the 3D printers would also need to be able to receive and process the large stl file (stl= STereoLithography), a file format commonly used for printing 3D models. This limitation is not insurmountable, but does require a concerted effort in development to overcome.

**Long printing times**
In terms of manufacturing time/printing speed in general, 3D jetting has the highest build speed, followed by laser lithography, laminating and extrusion in order of high to low speed.[47] An exceptional case is the more recently developed CLIP technique based on laser lithography that has achieved several orders of magnitude reduction in manufacturing time compared to SLA.[21] Printing time increases with increasing quality or resolution of the desired product. To print a 100 mm × 100 mm flat sheet membrane with pore size of 100 nm could potentially take several months and therefore substantial cost. Again, this needs to be addressed in improvements in AM technology.

### 3.2 Build material, support material, and mechanical properties
A range of materials can be printed by the currently available commercial AMs. Table 2 presents data from the material suppliers and printer manufacturers, including mechanical properties where available.

The mechanical properties of the 3D materials are process dependent and depend strongly on the direction in which they are tested.[48] Equipment manufacturers are often reluctant to supply material data (such as mechanical properties and composition), and comparison between material data is further complicated by the variation in measurement techniques. Some manufacturers supply data obtained from parts printed on their 3D printer, while others supply only data from tests on bulk samples of the source material. Nevertheless, this data
still provides useful information in terms of the relative order of magnitude of the mechanical properties that can be produced by the 3D printers.[49]

Additional issues include AM system and material compatibility with the desired product. For example, in extrusion-based AMs, the nozzle may be clogged by the material due to agglomeration of material and increased viscosity. Careful design of the membrane is required to avoid embedment of unused material within the membrane matrix. These trapped materials (liquid or loose powder) may be difficult or even impossible to remove after completion of AM.[8] In material jetting systems, which employ wax as the supporting material, the latter is printed as the negative region of the model (e.g. the pores of the membrane). The removal of wax is more difficult the smaller the gaps or pores printed. Potentially complete removal of wax from these negative regions may be problematic – however the extent of this potential problem has not yet been comprehensively studied for membranes. Fee et al. [50] implemented alternating warm water and cyclohexane washing for several hours to remove the wax in different printed porous media. However from the authors’ experience, when the pore size of the printed product is below 250 μm, removal of wax by successive washing of alternating solvents can be challenging for porous membranes.

Furthermore, stability of the printed photopolymers in solvents (water and organic solvents) as well as thermal stability are usually not available. When exposed to solvents or heating, the photopolymer may experience ‘swelling’ or morphological changes which results in final product that deviates from the original design. During the reviewing process of this work, the stability of the 3D printed spacers have been raised: it has been observed that the AM spacers break after long term soaking in water. The cause to this was not known, but could be due to the stability of the photoinitiators in the polymer materials. Other potential causes to this may be the incompatibility of the polymer with water, swelling or inaccuracy in 3D printing leading to micro cracks that propagate when exposed to solvents. Further development work and testing of AM materials is needed to help move towards stable and versatile AM membranes.

In terms of the desired characteristics for membrane fabrication (above), Table 2 shows that current AMs do not conventionally print with the wide range of common membrane materials that we currently use for fabricating membranes such as polyethersulfone and polyimide. Nevertheless, since membrane synthesis in AM has a completely different route to that of the phase inversion process, conventional membrane polymeric materials are not necessary and other photosensitive polymers with the desired properties can be used.

Many of the materials in Table 2 could potentially resist high pressure process environments or organic solvents (but this would need to be properly confirmed under realistic membrane test conditions). There is not enough information available in the literature currently on the implications of print support material and characteristics on AM membrane fabrication to determine which technique is superior or if there is a problem or not with having or not having a print support material in the build.

If other materials are required, then the solution would be to develop AMs with printing materials expanded to common polymer materials for membranes such as polyethersulfone, polyamide, polyimide and microporous organic polymers. Composite materials with sufficient mechanical strength need to be prepared to ensure that the membrane produced remains stable while the thickness is reduced. The printing material can also prepare the printed part for further post modification. For example, as a proof-of-concept, a vinyl-terminated initiator was added into UV curable resin for printing. The printed products which have the vinyl-groups that can be easily functionalized by growing polymer brushes via surface-initiated atom transfer radical polymerization.[51, 52] Furthermore, the polymer brushes would induce the formation of metal layers with excellent adhesion to the functionalized substrate via electroless plating (ELP) and the substrate can be etched away as needed.[53] Quick et al. developed a resin with thiol groups that can be employed for grafting of different maleimides via thiol-Michael addition reactions.[54] Inorganic membrane fabrication is also possible, with ceramic and metal printing AM processes having been developed. Most of the earlier techniques for printing ceramic-based materials (alumina, zirconia and gypsum) were using inkjet printing, which provides more flexibility in designing the composition of the binder and powder. It is also possible to replace the green precursor in
These findings were not targeting derived ceramics that are added with (SiOC, Si₃N₄ and SiC) ultraviolet (UV) jetting technique. The main idea of this method was to combine the ceramic powder together with the ultraviolet (UV)-curable resin, whereby each printed layer was cured by UV laser selective scanning on the ceramic suspension.[57] Moreover, HRL Laboratories has successfully printed many forms of ceramics (SiOC, Si₃N₄ and SiC) of varying compositions, complex shapes and cellular architecture by using polymer-derived ceramics that are added with a UV free-radical photo initiator. The pyrolysed polymer-derived ceramics were dense and exhibit a higher compressive strength than commercially available ceramic foams that their porous materials are similar to.[58] Although these findings were not targeting for membrane applications, they have indeed opened up more opportunistic paths for the printing of ceramic-based materials in the near future.

Table 2. AM materials and their properties. a

| Material | HDT (°C) (at 0.45 MPa) | HDT (°C) (at 1.82 MPa) | Tensile Modulus, E (MPa) | Tensile Elongation at break (%) | Flexural Modulus (MPa) |
|----------|------------------------|------------------------|--------------------------|-------------------------------|------------------------|
| Standard | ASTM D648 | ASTM D638 | ASTM D790 |
| Polymer  |           |           |           |
| ABS      | 55–104    | 50–100    | 28.2–75   | 1890–3650 | 1.3–40 | 1700–3240 |
| PLA      | 54–88     | 54–88     | 57–110    | 3309–3596.30 | 3.9–100 | 1972 |
| PA       | 50–188    | 44–188    | 28.0–55.9 | 8–6248   | 0.03–497.60 | 13–5040 |
| PET      | 71.8      | 65        | 18.13–31.14 | 554–2147 | 7.8–18 | 1840 |
| TPE      | N/A       | N/A       | 7–52      | 75–80    | 70–200 | N/A |
| PC       | 51–138    | 51–138    | 52–68     | 2000–3100 | 4–13 | 2100–3000 |
| PEI      | 186–216   | 186–216   | 71.60–97  | 2200–2804 | 1.3–9.5 | 2234–2926 |
| PP       | 42–102.60 | 37–84.50  | 17–53.8   | 553–2500 | 8–50 | 768–2450 |
| ASA      | 98        | 98        | 30–33     | 1950–2010 | 3–9 | 1630–1870 |
| PEEK     | N/A       | N/A       | 48–93     | 3530–4250 | 1.2–4.7 | 180–4100 |
| PPS      | N/A       | N/A       | 55–73     | 2100–2570 | 3–5.8 | 2200–3973 |
| Acrylic  | 47–88     | 45–88     | 32–80     | 1724–3500 | 7.7–25 | 1900–3500 |
| PMMA     | N/A       | N/A       | 3.7–4.3   | N/A      | N/A | N/A |
| Oxyacetane| 64        | 64        | 51        | 2000     | 8 | 2600 |
| HDPE     | N/A       | N/A       | 21        | 2000     | 5.5 | N/A |
| Rubber   | N/A       | N/A       | 0.8–5     | 0.7–9.2  | 45–293 | 5.9–7.8 |
| Silicone | N/A       | N/A       | 1.7       | 1.1      | 130 | N/A |
| Epoxy    | 46–250    | 46–250    | 26–85     | 1100–9200 | 2–25 | 1200–8900 |
| Composite|           |           |           |           |           |           |
| ABS-Carbon| 104      | 99        | 52        | N/A      | 2–3 | 7100 |
| ABS-PP   | 62–188    | 62–188    | 37–52.6   | 1517–1925 | 6.58–47 | 1310–1915 |
| ABS-PBT  | 46–54.5   | 45.9–53   | 33.8–53.60 | 2370–2880 | 6–20 | 2040–2370 |
| ABS-Acryl| 47        | 46        | 55–56     | 2860–2900 | 6–9 | 2410–2570 |
| ABS-PC   | 110–135   | 110–135   | 41        | 1900     | 6 | 1900 |
| PLA-Carbon| 56.2     | N/A       | 50        | 4711     | 1.88 | 9100 |
### 3.3 Costs

**High printing material cost**

The cost of the printing materials depends on the type of AM technique. For instance, photopolymers, such as those for stereolithography, cost ~USD200–300 per kilogram. For FDM prototyping, ABS costs ~USD350 per kilogram (or ~USD250 per kilogram as of the time of writing, from Stratasys website). However, unused material cannot be completely reclaimed and waste is generated with each build.[47] The material cost also vary with the quality of the material and in general, the material for a desktop 3D printer is much cheaper compared to the commercial grade. For example, the printing materials for a desktop FFF printer range from USD19/ kg to USD175/ kg.[59] The cost of material (not including exotic materials or precious minerals) from high to low is generally as follows: SLS> FDM> LOM> SLA> material jetting.[47]
**High potential membrane fabrication costs**

Current membrane modules have been estimated to cost about USD350 per square meter of membrane.[60] In comparison, the potential cost of using AM for membrane fabrication is comparably higher due to the requirement of much more complex machinery and membrane materials (as above) over conventional phase inversion step. The complex machinery requires more maintenance service and consumables. For instance, the laser sources or UV lights have limited lifespan and need to be replaced often. The cost would decrease as technologies improve but will most probably remain significantly higher than conventional membrane fabrication methods. Therefore, AM membranes will need to have separation characteristics in particular applications that outcompete conventional membranes so substantially that the cost savings of using them outweigh the additional cost of manufacturing them. These are likely to be applications where precise control over the membrane structure (pore shape, pore size distribution etc.) are advantageous. Therefore the use of the AM technique – as it currently stands – to design and fabricate membranes is unlikely to be competitive enough to replace existing membrane fabrication methods, but could potentially be applied in targeted applications or niche membrane market (such as in organic solvent systems), where bespoke membranes are required for a particular niche application and therefore require tailored design.

3.4 Implications

In terms of the desired characteristics for membrane fabrication (above), since AM of membranes is currently in its infancy, there is still much work to be done to make the technology cost competitive and comparable to phase inversion membrane fabrication – this is one of the main challenges and research goals going forward. For all of these reasons, only limited work on AM membranes has been done so far.

**4. WHAT HAS BEEN DONE SO FAR**

AM techniques for separation membrane applications is a relatively new area of research. Because of the limited materials available for printing and the high cost and limited hardware for obtaining nanometer resolution in 3D builds to produce practical membranes (as outlined in Section 3 above), most AM has focussed on membrane modules and membrane spacers (as covered in [18]). Limited studies have been published on using AM techniques to prepare membranes. Matthias Wessling’s group at RWTH Aachen is currently the most active one, working on a number of different AM membrane areas. They have printed a polydimethylsiloxane (PDMS) membrane using a DLP printer for gas-liquid contact by formulating a PDMS photoresist material for printing of silicone structures (Figure 3a).[16] The membrane design was based on ‘triply periodic minimal surfaces’ (TPMS).[61] Compared to standard PDMS membranes, the printed PDMS membranes showed similar selectivity but 15% lower permeability. This may be due to higher crosslinking density in the new membrane. Nevertheless, the printed membrane has a much lower permeance due to its thickness (840 µm).[16] An alternative approach to that is to print a negative mould of the desired membrane design and use this as a template for the membrane fabrication (Figure 3c). The Wessling group printed an acrylate-based sacrificial negative mould as the template for PDMS.[15] The mould was then backfilled with PDMS and later removed under alkaline conditions without impairing the PDMS membrane properties. The membrane architecture, also based on the TPMS model, has improved mass transfer performance over common hollow-fiber membranes with equal geometric parameters through CFD simulations.[15] However, the membrane is still quite thick (about 1 mm) compared to conventional membranes in order to withstand a pressure of 2 bar. To reduce the thickness, a support layer might be added to the design, resembling that of conventional phase inversion membranes. Nevertheless, both these studies have demonstrated the strength of AM techniques in making complex 3D geometries for membrane applications and its complete freedom in the design of the contactor interface geometry.[15, 16]

Besides AM techniques, conventional ink-jet printers have also been used to fabricate membranes.[17, 62-65] 3D features have been produced using ink-jet based printer at much lower cost than AM techniques.[66-68] Herein, membrane fabrication based on ink-jet printing, which may or may not possess 3D features are discussed. Badalov et al. used an inkjet printing technique to fabricate a patterned thin film composite membrane (Figure 3b). A fluorinated diamine monomer checkerboard pattern was printed on an ultrafiltration membrane pre-soaked in an aqueous solution of m-phenylenediamine (MPD). The membrane then underwent a conventional interfacial
polymerization step, by treating the membrane with trimesoyl chloride (TMC) in n-hexane. The patterned membrane showed improved permeate flux and salt rejection which could be due to the molecular size difference between the printed monomer and MPD, a difference in hydrophobicity between the two membranes or a positional variation of the fluorinated diamine which affects the hydrogen bonding.[17]

The same group also applied the same ink-jet printing technique to print multiple coating of MPD to an ultrafiltration membrane support, before application of TMC to form the polyamide layer. As the amount of printed MPD was increased (from 1 layer to 5 layers), the membrane salt rejection increased while the flux decreased. This was because of the increased polymer crosslinking and polyamide layer thickness with increasing number of coatings. The printing method introduced a new accurate technique to control the formation of polyamide, which does not require the step to remove excess liquid and could mean an overall more efficient fabrication process.[62]

Gao et al. [63] prepared a thin film membrane using a modified inkjet printer by controlled alternate printing of poly(allylamine hydrochloride) (PAH) and poly(styrenesulfonate) (PSS). The thickness of the bilayers was controlled by the number of printing cycles. Such thin films were also generated using a dip-coating based layer-by-layer (LbL) assembly and showed promising results as nanofiltration membranes.[64] Other nanostructured membranes prepared by LbL inkjet printing of PAH/PASS nanotubes and inkjet printing of poly(vinyl alcohol) (PVA) nanowires and nanotubes were also prepared. Compared to their dip-coated counterparts, the inkjet based LbL offers several advantages, including ease of production, material requirements, and most importantly, the ability to form chemically patterned functional thin films.[63]

Using the same inkjet printing approach, Gao et al. [65] prepared a multifunctional mosaic membrane by printing alternative domains of positively charged and negatively charged consisted of either poly(diallyldimethylammonium chloride) or poly(sodium 4-styrenesulfonate), on the surface of a polycarbonate track-etched membrane with 30 nm pores, producing a mosaic membrane that possessed an overall neutral charge (i.e. a membrane that had balanced coverage of positively and negatively charged domains). The mosaic membrane was capable of enriching the concentration of salt in the permeate side (i.e. negative salt rejection) which is useful in many established technologies that rely on selective transport of ionic solutes from solution.[65]

Figure 3. (a) 3D-printed PDMS membrane contactor. Gas flows horizontally from left to right while the bromothymol blue pH indicator is pumped vertically from the bottom to the top through the contactor. The colour change of the pH indicator from blue to yellow indicates the CO₂ transport over the membrane. Reproduced with permission from [16]. (b) Ink-jet coating of membrane. Checkerboard patterns of fluorinated diamine were printed on a pre-soaked ultrafiltration substrate followed by conventional interfacial polymerization of the polyamide. Reproduced with permission from [17]. (c) Preparation of 3D-PDMS membranes via a sacrificial resist. Step-by-step fabrication for the Schwarz-P geometry: rapid prototyping of the sacrificial mould, backfilling of the mold with PDMS followed by thermal curing, alkaline removal of the mold material and TPMS membrane under steady-state condition. The colour
change of the pH indicator from blue to yellow again indicates the CO\textsubscript{2} transport through the PDMS membrane. Reproduced with permission from [15].

Other than polymeric membranes, researchers from University of Twente attempted to print ceramic (alumina and zirconia) membranes by using a direct-based inkjet printing process.\textsuperscript{[69]} The printer was custom-made and can potentially be adapted for the SLS process by mounting a laser to the machine. It was demonstrated that the green parts can be printed by means of an ink-jet head. The green parts are then sintered in a separate sintering process. More work is still needed to improve the quality of the sintered product, as current post-sintered products were found to be very fragile.

Yao et al. fabricated a porous Al\textsubscript{2}O\textsubscript{3} by combining the concept of indirect 3D printing (layer thickness of 50 \textmu m or 100 \textmu m) and reaction bonded aluminium oxide (RBAO).\textsuperscript{[70]} Pure Al was used as the green body precursor, in which the printed Al tablets was sintered at 1600 °C in a muffle furnace. During the thermal process, oxidation of Al to Al\textsubscript{2}O\textsubscript{3} occurred at 660 °C, followed by the continuously formation of molten Al at higher temperature that filled the voids of the structure and reacted with oxygen to form Al\textsubscript{2}O\textsubscript{3}. The sintered products exhibited high porosity (~45%), remarkable flexural strength (~70 MPa) and reasonable dimensional change (~1-2 %). The pore size of the Al\textsubscript{2}O\textsubscript{3} body was not examined but this report could potentially be a good example for printing porous ceramic membranes in the future.

5. FUTURE POTENTIAL

The AM membranes produced so far hint at the possible membranes and developments that AM should enable. Looking to the future, much beyond these initial tests, the application of AM could potentially revolutionise the design and development of membrane system if AM technology can evolve beyond the current benchmarks and their inherent limitations in printing practical separation membranes outlined in Section 3. For example, three advantages not currently possible with conventional membrane fabrication techniques include:

**Wide capability.** Rapid prototyping processes provide significant advantages in terms of speed, efficiency and customization, when compared to traditional prototyping.\textsuperscript{[8]} However, conventional membrane synthesis such as the phase inversion method is, in general, comparably faster than 3D printing, when considering the rapid phase inversion step. Nevertheless, 3D printing has the capability to produce not only the membrane, but also the spacers and the entire membrane module, which may reduce the overall production time. Furthermore, unique membrane modules that improve mass transfer and mixing could be designed.

**Precision control over complex structures.** One limitation of the phase inversion method (and other common membrane fabrication methods such as interfacial polymerisation, sintering, coating etc.) is the inability to freely design complex geometries and internal features. AM on the other hand enables new ways of making membranes with little constraint on the designs of delicate features both internally and externally, with the use of 3D drawing tools. With AM, any membrane structure up to the highest resolution of the AM machines can be produced. Moreover, AM makes it possible to control the composition of two or more materials across the surface and interface during fabrication, allowing positional variations in physical properties and characteristics, namely, multiple alternating layers of materials or selective distribution of one material on another.\textsuperscript{[8]} So for example, membranes with structures to reduce fouling, to selectively channel the feed towards particular parts of the membrane and membrane material that separate a sub-set of molecules and another part with different properties that separate a different subset of molecules in the same sheet could be possible. A wide array of new membrane types, properties and possibilities are available when AM technology overcomes the current limitations of resolution and build time/speed, pushing us further into a paradigm where more and more our imagination could be a limitation rather than our ability to control the structure of the membrane.

**High fidelity.** In AM, the fabrication of membranes is based on the preformed design model. Therefore, the resulting prototype will be identical to the original model if printed in full accuracy. Compared to the traditional phase inversion method (and the other aforementioned methods), AM exhibits higher consistency in prototype quality and narrow surface pore size distribution can be attained. Taking a common phase inversion membrane
fabrication method as a prime example for comparison - non-solvent induced phase separation (NIPS) – poor quality is caused by the de-mixing of the polymer solution and non-solvent during phase inversion that is not directly controlled. Thus, the resulting phase inversion membrane always shows a distribution in pore sizes and irregularity in membrane structures. AM on the other hand, will always produce the membranes exactly as they were designed, even though the characteristics of the membranes may vary with certain specifications, such as material quality and accuracy of the AM printer.[71]

Therefore, despite the multiple challenges that need to be overcome, AM still holds great promise and exciting possibilities for membrane fabrication and design due to its unique advantages over conventional techniques. Since AM prints the predesigned CAD models, theoretically any shape or design can be produced within the capability of the 3D printers. The potential of the technique promises to unlock great possibilities in both membrane architecture as well as membrane module design and some of these possibilities are discussed below.

5.1 Biomimicry
The AM technique is particularly useful in recreating structures that resemble nature, i.e. a biomimicry approach. Natural selection has produced well-adapted structures and materials in living organisms over geological time. By applying a biomimicry approach, one could potentially find solutions to many engineering problems. In membrane separation techniques, issues such as mechanical strength, fouling, flux, and separation properties can potentially be improved via biomimicry.[72-74] To recreate natural structures, data obtained from computerized tomography and 3D scanners can be used to reconstruct nature’s architecture in CAD models.[8] The CAD models can be further manipulated or rescaled to suit the needs for specific applications before printing.

5.2 New fabrication methods for hybrid membranes
Hybrid membranes are here defined as those possessing a distinct phase, which determines the membrane’s selectivity and permeability, embedded into a second phase providing structural support and integrity, so as to create a continuous transport channel across the separating layer. These hybrid membranes are distinct from mixed-matrix membranes where a second phase is dispersed at relatively low concentration in the selective layer of a thin film composite membrane to provide, for example, some anti-fouling resistance or modest increases in permeation. So-called vertically-aligned carbon nanotube membranes are a good example, though not yet scalable, of a hybrid membrane where the nanotubes provide both the permeating pathway and selectivity by size exclusion and the polymer matrix embedding the tubes does not play any active role in the separation process.[75]

Many challenges remain, however, in the preparation of hybrid membranes, including the alignment of the transport channels in both the support and the separating layers, the adhesion between the different phases and with the support, and fabrication methods that are scalable and economically competitive with current technology. Here, AM can play a key role in shifting the paradigm in membrane fabrication, offering the opportunity to print all of the membrane as a single monolithic piece, using multi-materials and complex configurations, all of which can be accurately designed. This approach can also potentially overcome the current AM limitation in terms of resolution, where microporous materials could be integrated into the printing materials. The product therefore would consist of currently achievable micrometer-size features but with microporosity of the porous components. Specifically, AM can provide a tailored scaffold-like membrane made up by polymer and porous nanomaterials. A recent review on the AM of multifunctional nanocomposites for other applications such as microelectromechanical systems, microfluidics, microelectronics and tissue engineering may be of interest to the readers.[25]

5.3 Post processing of AM membranes
As mentioned in Section 3, with current AM technologies, one could print at a resolution of ~100 nm at build size up to 100 × 100 mm² (with a Photonic Professional GT, Nanoscribe). Further details can be gained through post-processing steps, e.g. to create smaller pores. For instance, micro- and nanomachining can be used on printed dense membranes. Various milling techniques are available including focused ion beam (FIB)[42] and scanning probe nanomachining (SPM).[76] However, milling techniques have limited practicability for large scale membrane production. See also ‘subtractive manufacturing below’ for other techniques. Solvent can also be potentially introduced to selectively polish the membrane to achieve smaller pore sizes. He et al. [77] introduced
a simple method, referred to as scanning printing polishing casting (SPPC) for the fabrication of low cost soft tissue prostheses. A chemical polishing method is used to polish the casting mold to acquire a smooth surface.

5.4 Membrane surface patterning
Surface patterning of membrane can be tailored to reduce colloidal or protein deposition during active filtration by changing surface roughness or aiming at improving mixing. Current membrane surface patterning is achieved using the nanoinprint lithography (NIL) technique [78] to create submicron surface patterns on a commercial ultrafiltration membrane.[79, 80] Apart from that, surface patterning can also be applied to a thin film composite membrane, as demonstrated by [81, 82]. More details on the use of NIL for membrane surface patterning can be found in the review by Ding et al.[83] On the other hand, surface patterning of membranes can potentially be achieved using 3D printing techniques. One advantage of AM over NIL is the ability to create surface patterning on any types of membranes including hollow fibres, which can be difficult to pattern via NIL.

5.5 AM membrane as substrate
The printed membrane can also be used as a novel substrate for functional materials such as (1) metals, (2) metal oxides (e.g. TiO₂, ZnO), ceramics (e.g. Al₂O₃, SiO₂), (3) porous materials (zeolite, metal-organic framework (MOF), covalent organic framework (COF), zeolitic imidazolate framework (ZIF), porous organic polymers, and porous molecular solids],[84] (4) carbon-based material (graphene, graphene oxide (GO) and carbon nanotubes (CNT)),[85, 86] and (5) other polymers including hydrogels.[87] Figure 4 and Table 3 summarize the potential techniques for transferring functional materials on the printed substrate. Readers are referred to several review articles and books of the respective techniques for details (see [88-93]). The suitability of the aforementioned techniques depends upon several factors, i.e. the substance to be deposited, the nature of the substrate material, and the film structure, thickness and distribution.[91]

Table 3. Potential techniques for transferring functional materials on the printed substrate.

| Functional materials                  | Techniques                                      | Ref |
|--------------------------------------|-------------------------------------------------|-----|
| Metal and metal oxides               | Atomic layer deposition (ALD)                   | [94]| |
|                                      | Chemical vapour deposition (CVD)                | [95]| |
|                                      | Galvanization technique (LIGA process, a German acronym for Lithography, Galvanization and Abformung (molding)) | [96]| |
| Micro/mesoporous materials           | Contra-diffusion method                         | [97]| |
|                                      | Direct growth                                   | [98]| |
|                                      | Secondary growth                                | [98]| |
|                                      | Vacuum filtration                               | [99]| |
|                                      | Vacuum deposition                               | [91]| |
|                                      | Dip-coating                                     | [100]| |
|                                      | Spin-coating                                    | [101]| |
|                                      | Hydrothermal growth                             | [102]| |
|                                      | Electrospinning                                 | [89]| |
| Polymer                              | Layer-by-layer assembly                         | [103]| |
|                                      | Interfacial polymerization                      | [93]| |

5.6 Novel membrane shapes
Most common membrane shapes are flat sheets or tubular/hollow fibres, dictated by the techniques by which we can economically and easily manufacture membranes. However with AM, this is not necessary – any membrane shape could be manufactured, allowing features that enable improved mass transfer (as per the work outlined in Section 3), decreased concentration polarisation and fouling, and enhanced selectivity. The possibilities just need to be designed and they can be printed.

5.7 Novel module design
These novel membrane shapes would also need novel membrane modules. Another promising feature of AM approach is that the 3D printer cannot only be used to fabricate the membrane, but the entire module, producing the membrane, spacers and casing all-in-one, using different materials for each. The use of AM technologies has
also been long explored in the design of membrane spacer ultimately to improve mass transfer.[104, 105] AM approach allows the engineering of novel membrane modules which may be challenging to produce using conventional techniques. The approach also avoids conventional module manufacturing step which may degrade the membrane during module production phase.

6. ALTERNATIVE RELATED TECHNOLOGIES TO 3D PRINTING

So far this perspective has outlined the virtues and limitations of AM for membrane fabrication and has outlined how potentially these limitations can be overcome so that only the virtues remain. However, to provide balance to this, it must be noted that AM is not the only method for producing structure-controlled membranes. Alternative technologies to AM, either instead of or in combination with AM, may also produce the required outcomes. To do this, we will briefly outline the two main related and competing systems, which are: other printing techniques (other than AM) and subtractive manufacturing.

6.1 Other printing techniques

These novel printing techniques include electrospaying,[106] transfer printing[107] and screen printing[108]. The techniques introduced here are currently used to design nanostructures, thin films and microdevices but have not yet been widely applied to fabricate membranes. These could potentially be the basis of AM methods of the future to address the current limitations. Furthermore, inkjet based printing, which is based on a modified desktop ink printer rather than a 3D printer, can also be used for membrane design.[63]

**Electrospray printing** (Figure 5a), also known as electrohydrodynamic spraying is a common manufacturing process for tailoring nanoarchitectures of materials, including nanoparticles, nanoporous fibres as well as functional thin film deposition.[106] It is a method of liquid atomization via the use of electrical forces, whereby the liquid at the outlet of a nozzle is subjected to an electrical shear stress by maintaining high electric potential on the nozzle. The technique can create nanometre to micrometre size droplets by controlling the flow rate and voltage applied. A dual electrospray (Figure 5b) can also be used to deposit materials that are thermodynamically immiscible.[109] Jun-Muk *et al.*[109] demonstrated the use of a dual electrospray technique to produce a Nafion/sBlock (multiblock sulfonated hydrocarbon copolymer) blends that are difficult to produce with conventional blending methods due to their large miscibility difference.

**Transfer printing** is a technique to pattern a material onto a substrate and then transferring it onto a second one.[107] It relies on the fact that adhesion of an object to an elastomeric support is rate-sensitive, i.e. depends on the rate at which the elastomeric holder or stamp is peeled away from a flat surface. Fast peeling (typically ~ 100 mm s⁻¹) leads to adhesion strong enough to carry adhered objects away from the surface, whereas slow peeling (~ 1 mm s⁻¹) causes the objects to adhere preferentially to the device substrate, thus leaving such objects behind. Figure 5c shows an example of the technique, which transfers the microstructures (yellow) from a donor substrate (blue) to another substrate (red) with the use of an elastomeric stamp.[110] Recently features below 10 nm have been produced.[111]

**Screen printing** (Figure 5d) is a well-established technique which uses a mesh screen to transfer ink onto a substrate in a given pattern. The ink is placed on top of a thin screen consisting predesigned pattern of open apertures that the ink is forced through with a blade or squeegee. The quality of screen printed films depends on the mesh size, ink rheology and the substrate, of which ink rheology has the strongest influence and therefore is the most important parameter to control.[108] Also, screen-printed films are usually much thicker than other film preparation method such as electrospraying, typically from 400 nm [112] to 500 μm.[113]

**Inkjet printing** is a technology developed in the 70s that offers a rapid method for depositing precise amounts of materials (usually inks) to specific locations on a substrate (usually paper).[114] Only more recently its use has been extended beyond the printing of graphical images, towards printing functional materials.[115] Its use for membrane design was discussed in Section 4.
6.2 Subtractive manufacturing
Depending on the membrane’s composition and requirements, the alternative to additive manufacturing, known as subtractive manufacturing, may be viable. Subtractive manufacturing, which is a top-down approach, uses one of or a combination of mechanical, electromagnetic, and chemical processes to selectively remove material from a workpiece. The individual techniques involved are quite complex and can be specialised to specific processes. These methods are alternative or more often complementary to AM and could potentially offer better results than AM in some instances. Furthermore, complex shapes can sometimes be achieved through a combination of subtractive manufacturing steps intertwined with additive techniques such as deposition. However, subtractive manufacturing remains significantly more limited than AM with respect to the possible geometries that can be achieved (as the structure wanted has to have features that are surface accessible – something not required for and an advantage of AM). In membrane fabrication, subtractive manufacturing techniques such as mechanical micromachining, laser drilling, lithography, and etching techniques can be particularly useful in patterning and creating through-holes in a membrane and an overview of the techniques is given below.
Figure 4. Potential techniques for transferring functional materials on the printed substrate. (a) atomic layer deposition (ALD),[116] (b) chemical vapor deposition (CVD),[95] (c) LIGA method process (a German acronym for Lithography, Galvanization and Abformung (molding)),[98] (d) dip-coating,[117] (e) spin-coating,[117] (f) direct growth (on a chemically-modified substrate),[118] (g) contra-diffusion,[97] (h) vacuum filtration followed by secondary growth,[119] (i) hydrothermal growth,[120] (j) electrospinning,[89] (k) electrodeposition,[121] (l) vacuum deposition,[97] (m) interfacial polymerization,[122] and (n) layer-by-layer assembly.[123]
**Mechanical micromachining** is the traditional process of physically removing material through the direct contact of a tool with the workpiece done on submillimetre scale. There are many different tools and possible geometries available, ranging from diamond coated milling and drilling bits to large single crystal diamond milling bits for more brittle applications.[124] For applications where the workpiece’s material properties are not conducive to direct machining, there is also laser assisted micromachining where localised laser heating modifies the workpiece’s material properties to facilitate the mechanical micromachining.[125] Currently, the lower limit for the diameter of the tools is around 100–200 µm. Some of the drawbacks to mechanical machining are tool wear (which increases with higher aspect ratio cuts due to tool runout), large areas of workpiece hardening from the heat affected zone, potential surface contamination from the direct contact of the workpiece with the tool, and the intricacies of the mechanical setup that require stabilizing the rotating tool and rigidly supporting the workpiece.

**Laser drilling** is a versatile technique commonly used in many industrial applications on many different workpiece compositions for over four decades, and as such there are many review articles written both on the relevant physical processes and the practical applications.[125, 126] Laser drilling works by imparting electromagnetic radiation from the laser onto the workpiece and removing material by thermally heating a localised zone. The size of the zone, the rate of material loss, and its mechanism (either melt or vaporization) are controlled by the laser’s pulse width and peak and average power densities. Lasers with pulses in the sub picosecond range have been shown to be capable of removing material with significantly smaller heat-affected zones when compared to mechanical micromachining.[125] The limit for the diameter of a through hole can be as low as 1 µm for thin films, but is highly dependent on the material’s thickness and composition, as well as the laser parameters. The drawbacks to laser micromachining are tapering of the through-hole diameter and the potential for material recasting possibly in undesirable phases.

**Lithography**, with respect to manufacturing, is a broad term that generally refers to removing material from a workpiece by directing energetic charged particles at the surface of the workpiece in a controlled pattern.

**Figure 5.** Various other printing techniques. (a) electrospraying,[106] (b) dual electrospraying,[109] (c) transfer printing,[107] and (d) screen printing.[108]
Photolithography (using electromagnetic radiation instead of charged particles) and electron beam lithography do not directly remove the material but instead modify the material, which can be used as a mask for later etching and will be discussed later. Using ions or ion clusters to remove the material on the other hand, is known as focused ion beam (FIB) lithography and it is now possible to achieve features below 10 nm scale.[127] Ion clusters have significantly reduced an earlier problem of ion implantation into the workpiece. The downside is that the process is time consuming and expensive and it currently does not realistically scale up to macroscopic membrane fabrication.

**Etching** is a technique that selectively removes material via chemical reactions. Masks are applied over parts of the workpiece to reduce the rate of material removal. Electron beam lithography and photolithography are used to create the masks, which are patterns on the surface of the workpiece that have selective material properties. The difference in material properties is exploited by placing the material in a chemically reactive environment for controlled times, allowing for varying degrees of interaction with the workpiece, and ultimately selectively removing material. Most chemically reactive processes like etching are isotropic and it is hard to generate high aspect ratio features like a through hole for a membrane. Chemical anisotropic methods are well established for specific materials, such as silicon, but are limited by the type of geometry they can produce. Reactive ion etching (RIE) is a highly anisotropic technique that can produce high aspect ratio features in a variety of materials. [128] Like most etching methods, masks are required to pattern the surface, somewhat limiting its applicability to large scale. Furthermore, RIE requires expensive high power sources and vacuum, also complicating scalability.

![Images of different microstructures produced by various methods.](image)

**Figure 6.** (a) Trapezoid microgrooves produced by mechanical micromachining with a diamond tool,[124] (b) gold stars on a silicon substrate fabricated by electron beam lithography (image courtesy of [http://www.nano.aau.dk/]), (c) silicon nitride with square holes fabricated by laser micro drilling (image courtesy of [http://www.oxfordlasers.com/]), and (d) silicon nanopost structures produced by deep reactive ion etching.[129]

7. CONCLUSIONS

7.1 Requirements for a 3D Printer for separation membranes

An ideal printer for separation membranes would have high accuracy and resolution to produce membranes with unique features down to the nanoscale, and high printing speed and build size for scale-up production of membranes. We have illustrated that current AM techniques are not cost-effective for membrane fabrication and
are projected to remain non-competitive to conventional membrane fabrication techniques due to the requirement of complex printing technologies and materials in the short/medium term. However, future AM techniques may be targeted for niche membrane markets whereby specific membrane design requirements are needed. Current printing technology is able to print dense membranes as well as porous one with resolutions from ~100 nm, thus are unsuitable for ultrafiltration and nanofiltration. Post-processing or modification of the membranes is therefore required after printing the membrane to achieve the desired pore size. In terms of printing speed and build size, further improvements of 3D printers to print fine structures at large scale in a short time is important to compete with currently available membrane fabrication techniques.

It is clear that the use of AM for membrane fabrication is highly dependent on the further development of AM techniques. At present, high resolution printing can only be achieved by laser-based methods, with resolution is dependent on the laser source. The recent development of 1.5 Å wavelength lasers could potentially improve the resolution in the future. However, these printers have higher overall costs than lower resolution models, have limited build size and very long printing times. A more cost-effective approach could be the improvement of material jetting and FFF-based printers. The smallest feature size of printed dots is determined by the deposition area of printed droplets. The deposition of single droplet involves the process of ejection from the nozzle, impact on the substrate and ultimately spreading or retracing on the surface. These processes are affected by the wettability of substrate, the properties of the printing material as well as the droplet generation techniques. In general, engineering a hydrophobic surface and low surface energy would reduce the tendency to spread, reducing droplet diameter, and improving resolution. It is anticipated that the surface modification of each layer before the deposition of subsequent layer would allow better control over the spreading of the droplet and therefore the printer’s resolution. Changing the formulation of the printing material can improve the ejecting process (avoid clogging) and also the resolution of the printed patterns, by limiting material spread on the printed surface. New printing apparatuses can also potentially solve the resolution vs cost and print size/time problems – for example electrohydrodynamic jet printing, jet focusing by hydrodynamic and pyro-electrohydrodynamic shooting are potential future technologies that could enable sub-micrometre resolution for material jetting printers. These future developments could help unlock the potential of AM for membrane fabrication.

### 7.2 Materials for separation membranes

We have identified that current printing materials are limited, restricted to specific AM technologies and have little overlap with the current materials used for membrane fabrication. This is not necessarily a problem considering that AM membranes are likely to be initially for niche applications that would be optimised for the printing resolution and materials currently available. Future development in the AM field should not only focus on new printing material development, but also on expanding the use of existing printing materials to a wider range of AM technology. Printing materials need to be expanded to common materials for membranes such as polyethersulfone, polyamide, polyeimide and potentially microporous organic polymers. Composite materials with sufficient mechanical strength are to be prepared to ensure that the membrane produced remains stable while the thickness is reduced. The printing material can also be used to prepare the printed part for further post modification. The development of both printing materials and AM techniques are equally important to drive the application of AM techniques in membrane fabrication.

We hope that this perspective provides a clear insight into how AM techniques could be employed in the area of membrane science and technology and catalyse the development of AM techniques targeted for membrane systems. The use of 3D printing in membrane systems should see continued growth in near future. Either alone or in combination with other manufacturing methods, it is clear that AM has the potential to provide a unique set of membranes that will extend the possibilities of membrane-based separations beyond the current state-of-the-art.
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Figure 1. Schematic summary of AM techniques. Acronyms: stereolithography (SLA), two-photon polymerization (TPP), continuous liquid interface production (CLIP), selective laser sintering (SLS), fused deposition modelling (FDM), direct writing assembly (DWA), laminated object manufacturing (LOM), and selective deposition lamination (SDL). Note: DWA may also use liquid as the material.

Figure 2. Key properties of 3D printing techniques.

Figure 3. (a) 3D-printed PDMS membrane contactor. Gas flows horizontally from left to right while the bromothymol blue pH indicator is pumped vertically from the bottom to the top through the contactor. The colour change of the pH indicator from blue to yellow indicates the CO₂ transport over the membrane. Reproduced with permission from [16]. (b) Ink-jet coating of membrane. Checkerboard patterns of fluorinated diamine were printed on a pre-soaked ultrafiltration substrate followed by conventional interfacial polymerization of the polyamide. Reproduced with permission from [17]. (c) Preparation of 3D-PDMS membranes via a sacrificial resist. Step-by-step fabrication for the Schwarz-P geometry: rapid prototyping of the sacrificial mould, backfilling of the mold with PDMS followed by thermal curing, alkaline removal of the mold material and TPMS membrane under steady-state condition. The colour change of the pH indicator from blue to yellow again indicates the CO₂ transport through the PDMS membrane. Reproduced with permission from [15].

Figure 4. Potential techniques for transferring functional materials on the printed substrate. (a) atomic layer deposition (ALD),[116] (b) chemical vapour deposition (CVD),[95] (c) LIGA method process (a German acronym for Lithography, Galvanization and Abformung (molding)),[98] (d) dip-coating,[117] (e) spin-coating,[117] (f) direct growth (on a chemically-modified substrate),[118] (g) contra-diffusion,[97] (h) vacuum filtration followed by secondary growth,[119] (i) hydrothermal growth,[120] (j) electrospinning,[89] (k) electrodeposition,[121] (l) vacuum deposition,[97] (m) interfacial polymerization,[122] and (n) layer-by-layer assembly.[123]

Figure 5. Various other printing techniques. (a) electrospaying,[106] (b) dual electrospaying,[109] (c) transfer printing,[107] and (d) screen printing.[108]

List of Tables

Table 1. Specifications, materials, advantage and disadvantage of AM by various manufacturers.

Table 2. AM materials and their properties.

Table 3. Potential techniques for transferring functional materials on the printed substrate.