2022 Roadmap on 3D Printing for Energy

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ROADMAP

2022 roadmap on 3D printing for energy

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Keywords: 3D printing, additive manufacturing, fuel cells, solar cells, thermoelectrics, batteries, supercapacitors

Abstract
The energy transition is one of the main challenges of our society and therefore a major driver for the scientific community. To ensure a smart transition to a sustainable future energy scenario different technologies such as energy harvesting using solar cells or windmills and chemical storage in batteries, super-capacitors or hydrogen have to be developed and ultimately deployed. New fabrication approaches based on additive manufacturing and the digitalization of the industrial processes increase the potential to achieve highly efficient and smart technologies required to increase the competitiveness of clean energy technologies against fossil fuels. In this frame, the present roadmap highlights the tremendous potential of 3D printing as a new route to fully automate the manufacturing of energy devices designed as digital files. This article gives numerous guidelines to maximize the performance and efficiency of the next generation of 3D printed devices for the energy transition while reducing the waste of critical raw materials. In particular, the paper is focused on the current status, present challenges and the expected and required advances of 3D printing for the fabrication of the most relevant energy technologies such as fuel cells and electrolyzers, batteries, solar cells, super-capacitors, thermoelectric generators, chemical reactors and turbomachinery.
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1. Introduction

Albert Tarancón¹,², Marc Torrell¹ and Vincenzo Esposito²,³
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The sustainable energy transition is arguably the most crucial challenge of our society after two centuries of dependence on polluting fossil fuels. Accordingly, a global strategy based on the mass deployment of clean and efficient energy generation technologies and large-scale energy storage solutions (coupled to intermittent renewable sources) has been gaining importance in recent years. Among others, energy harvesting using solar cells or windmills and chemical storage in batteries, supercaps or hydrogen are now considered key future technologies for such a transition. Most of these technologies demonstrated their potential benefits a few decades ago and are still under development. Therefore, improving their performance and durability still represents the research community’s primary goal, but due to mass deployment, the exploration of suitable manufacturing strategies has also been accelerated. In this regard, new fabrication approaches based on the manufacturing industry’s digitalization have brought new perspectives that can be crucial to achieving the required performance and the necessary competitiveness of these energy technologies against fossil fuels.

In particular, 3D printing represents a new route for fully automatic additive manufacturing of three-dimensional objects designed as digital files. 3D printing is based on different deposition processes that reduce the amount of waste, which is exceptionally advantageous when involving critical raw materials such as those typically employed in energy technologies, e.g. cobalt, rare-earth elements or noble metals. Moreover, as an additive manufacturing method, 3D printing intrinsically provides a fresh approach to materialize never explored concepts based on a high geometrical, material and functional complexity [1–3]. The recent development of printable feedstock for energy applications supported the first breakthroughs. Some disruptive examples are fuel cells and thermoelectric generators with complex architectures [4, 5], the creation of highly reactive interfaces and surfaces for chemical and electrochemical systems [6, 7], the fabrication of parts with graded digital materials for turbomachinery [8] and reactors with embedded functionalities [9] (see figure 1). These advances are just the beginning of a collection of innovations that will significantly benefit from using powerful optimisation design tools based on artificial intelligence approaches and multi-physics simulations [10].

This roadmap aims to define the guidelines to maximize the impact of the 3D printing revolution on the next generation of devices for the energy transition. It also outlines the current status, challenges and required advances in Science and Technology for a series of power generation technologies (fuel cells, solar cells, thermoelectric generators and turbomachinery) and energy storage technologies (electrolysers, batteries and supercapacitors). Finally, the roadmap discusses the role of 3D printing in improving the mass and heat transfer to improve the energy efficiency of chemical reactors (CO₂ conversion) and novel cooling systems. Tables 1 and 2 list the materials and techniques described all along the roadmap as well as the key performance indicators targeted for all the energy technologies, respectively. With this document, the authors intend to provide a valuable tool for researchers, technology developers, and policymakers when defining their strategies for the energy sector’s future.
Figure 1. Main advantages of 3D printing for the energy technologies covered in this roadmap.

Table 1. Summary of the main materials and 3D printing technologies for the reviewed applications considered in the roadmap.

<table>
<thead>
<tr>
<th>Application</th>
<th>Materials</th>
<th>3DP technology</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel cells and electrolyser</td>
<td>SOFC: stabilized-zirconia electrolytes, electrode materials (lanthanum-based perovskite oxides and Ni-based composites), glass sealants PEM: polymer electrolytes (nafton) and electrodes (precious metals), metallic interconnects (stainless steel)</td>
<td>SLA, EFF, DIW</td>
</tr>
<tr>
<td>Solar cells</td>
<td>Current collection (silver, copper, tin, indium), supports (polymers), cells (P3HT: PCBM, organic perovskites, CIGS)</td>
<td>DIW, R2R, IL</td>
</tr>
<tr>
<td>Thermoelectric</td>
<td>Bi$_2$Te$_3$, Bi$_2$SbTe, Cu$_2$Se, PbTe</td>
<td>EFF, DIW, SLS, SLA</td>
</tr>
<tr>
<td>Batteries</td>
<td>Polymeric electrolytes (PVDF-co-HFP), electrodes (LiFePO$_4$-LPF, Li$_4$Ti$<em>5$O$</em>{12}$-LTO, composites with graphene oxide)</td>
<td>DIW, EFF</td>
</tr>
<tr>
<td>Supercapacitors</td>
<td>Polymeric electrolytes (KOH/polyvinyl alcohol), Electrodes (activated carbon, Ti$_3$C$_2$Tx MXene nanosheets, manganese dioxide nanowire, silver nanowires, and fullerene), current collection (Ag nanoparticulate), housing (polypropylene)</td>
<td>DIW, EFF</td>
</tr>
<tr>
<td>Turbomachinery</td>
<td>Ti-Alloys, Ni-base Superalloys, High Temperature Fe-base alloys, Intermetallics based on Ti or Fe</td>
<td>DED, SLS</td>
</tr>
<tr>
<td>Chemical reactors</td>
<td>Reactor (stainless steel, alumina), catalyst support (metal oxides), catalyst (precious metals)</td>
<td>DIW, DLP, EFF</td>
</tr>
<tr>
<td>Solid state refrigerators</td>
<td>Ferroelectric/ferromagnetic/ferroelastic caloric materials</td>
<td>SLS, DED, EFF, DIW, SLA</td>
</tr>
<tr>
<td>CO$_2$ capture and separator</td>
<td>High thermal conductivity metals or alloys (Aluminium AlSi10Mg)</td>
<td>SLS</td>
</tr>
<tr>
<td>Cooling electronics</td>
<td>High thermal conductivity metals or alloys (AlSi10Mg, Al 6061, CuNi2SiCr) and polymer composites</td>
<td>SLS</td>
</tr>
</tbody>
</table>

* SLA: stereolithography; DIW: direct inkjet writing; R2R: roll-to-roll; IL: imprint lithography; EFF: extrusion free forming; SLS: selective laser sintering; DED: directed energy deposition.
Table 2. Target key performance indicators for the different energy technologies covered in this roadmap.

<table>
<thead>
<tr>
<th>Application</th>
<th>Target key performance indicators</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel cells and electrolyser</td>
<td>Power density &gt; 1 W cm$^{-2}$</td>
</tr>
<tr>
<td>Solar cells</td>
<td>Power density &gt; 0.02 W cm$^{-2}$</td>
</tr>
<tr>
<td>Thermoelectrics</td>
<td>ZT = 0.9–1.4</td>
</tr>
<tr>
<td>Batteries</td>
<td>Specific energy: 250 Wh kg$^{-1}$</td>
</tr>
<tr>
<td>Supercapacitors</td>
<td>Specific energy: 5–15 Wh kg$^{-1}$</td>
</tr>
<tr>
<td>Turbomachinery</td>
<td>Highly complex multi-scale geometries</td>
</tr>
<tr>
<td>Chemical reactors</td>
<td>Mass and heat transfer: Sh: 100–400; Nu: 100</td>
</tr>
<tr>
<td>Solid state refrigerators</td>
<td>Adiabatic temperature change (ATC) &gt; 3 K, coefficient of performance (COP) &gt; 15%</td>
</tr>
<tr>
<td>CO$_2$ capture and separation</td>
<td>Surface area &gt; 250 m$^2$ m$^{-3}$, CO$_2$ capture &gt; 20%</td>
</tr>
<tr>
<td>Cooling electronics</td>
<td>$k &gt; 250$ W mK$^{-1}$, $d &lt; 100–200$ mm features</td>
</tr>
<tr>
<td></td>
<td>Rtd &lt; 0.1–0.2 W K$^{-1}$</td>
</tr>
</tbody>
</table>
2. 3D printing of fuel cells and electrolyzers

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Status

Fuel and electrolysis cells are electrochemical energy devices able to convert fuel into electricity for power generation (fuel cell mode) and electricity into gas for energy storage (electrolysis mode), respectively. Among other types of cells, the most promising technologies are polymer exchange membrane (PEM) and solid oxide cells (SOCs) according to the polymeric or ceramic nature of the electrolyte. Independently on the type of cell, PEM and SOC technologies are based on complex multilayer structures mainly consisting of an anode, an electrolyte and a cathode ultimately stacked using interconnect plates and sealants to sum the power of individual cells by connection in series or parallel. This multilayered structure that combines functional and structural materials makes 3D printing suitable for their deposition in the form of separate layers as well as for the fabrication of entire cells and components that, eventually, give rise to complete stacks.

3D printing has been extensively used in PEM and SOC technologies for depositing thin layers of the main components of the cells such as electrolytes, functional electrodes or catalysts over conventional substrates \cite{1,11}. Direct printing of ceramic \cite{12} and polymeric thin electrolytes \cite{13} has been progressively extended the activity on single-layer deposition to multilayer functional structures that, in the particular case of SOCs, ultimately led to fully printed devices \cite{14,15}. This successful multi-layering approach resulted in an enhancement of the individual cell performance based on the beneficial increase of the complexity of the materials introduced by 3D printing, e.g. using graded compositions or functional layers \cite{1,16}. However, thin-film layer-by-layer deposition techniques such as inkjet printing do not allow the fabrication of complex geometries (presenting high aspect ratio). This limits the beneficial effects of increasing shape and hierarchic complexity reachable by other 3D printing methods. In this regard, there are not examples of self-supported fully printed PEM or SOC cells with complex shapes. This is likely due to the lack of knowledge in high-aspect-ratio 3D printing of relevant functional materials such as ionic conductors either polymeric or ceramic. Only recent advances in stereolithography and dynamic light processing (DLP) printing of ceramic ionic conductors such as yttria-stabilized zirconia has changed the perspective, just for SOCs, opening the door for new architectures \cite{5} (figure 2(a)). In the case of PEM cells, due to few works on the direct deposition of the electrolyte, complex shapes are only being explored for the structural components such as interconnect metallic plates with the main goal of optimising the gas and water flow distribution while minimising the contact resistance \cite{11,17} (figure 2(b)).

Increasing the active areas of the different layers with enhanced interfaces and the introduction of hierarchical and shape complexity of fuel and electrolysis cells will substantially increase their current power and energy densities converting 3D structured PEM and SOC cells in the next generation of high performing devices.

Current and future challenges

Although PEM and SOC are of such a different nature as polymeric and ceramic, most of the current and future challenges facing the 3D printing of fuel cells and electrolyzers are shared by the two technologies. In both cases, the main challenge is to prove that 3D printing can improve the performance, durability and applicability of conventional cells by depositing enhanced layers, developing advanced interfaces or enabling new shapes and configurations using, in a first stage, only state-of-the-art materials. It is important to remark the tremendous potential progress in the field based on materials that were optimized for decades in PEM and SOC if 3D printing fully deploys their uniqueness in introducing materials, hierarchical and shape complexity (figure 3). Enhanced cells based on compositionally graded electrodes, fractal electrode-electrolyte interfaces or topologically optimized designs will be examples of revolutionary devices based on SoA materials but only reachable by 3D printing. In the case of PEM cells, improved multiscale graded interfaces will potentially solve one of the major problems of this technology, such as the interfacial contact resistances.

In the mid-term, it would be desirable to manufacture self-supported fully printed advanced cells and, ultimately, complete stacks solely enabled by the new manufacturing routes. This approach will open the way for revolutionary monolithic ultralight concepts that will include functional components such as current collectors, gas distribution channels, catalytic reaction chambers or manifolds. Embedded functionalities will potentially solve current critical issues related to high contact resistances, unbalanced gas and water flow.
distribution, low heat transfer and thermal coupling of auxiliary processes or the presence of multiple critical joints and sealing points. In the particular case of SOCs, novel cell geometries for increasing the thermal shock resistance by design will open the technology to portable power applications. At the same time, a monolithic stack approach will facilitate the development of simple high-pressure systems.

As soon as enhanced and unique designs are a reality, the focus should be on the estimation of the advantages of the new manufacturing technologies in terms of cost-effectiveness, energy efficiency and use of critical raw materials either coupled to conventional manufacturing methods (for the deposition of specific improved layers, for instance) or as single fabrication technologies of complete devices. This progress will allow the entire community to quantify the real impact of 3D printing technologies on the fabrication of PEM and SOC cells and systems and the possibility of driving a new revolution in the energy market.
Advances in science and technology to meet challenges
To reach 3D printed enhanced PEM and SOC cells, first, it is necessary to increase the portfolio of printable functional materials such as ceramic and polymeric ionic conductors, e.g. yttria-stabilized zirconia or Nafion®, and associated composites. Complementary, high-aspect-ratio printing methods (beyond inkjet deposited thin films) should be addressed for these materials to develop functional supports that enable fully printed cells and stacks with novel architectures of commercial size. Since different materials with different microstructures are required within a device, e.g. metallic plates and polymeric electrolytes in PEM or dense electrolytes and porous electrodes in SOC, the final goal of printing full cell or stacks will involve the use of the most suitable printing technique for each layer. This multi-material hybrid printing is still in its infancy, and further work is required to reach an optimum level of robustness. Moreover, this approach will require dealing with printing and post-deposition treatments of dissimilar materials, which could be especially critical for the needed co-sintering step in multilayer ceramics for SOCs. To completely solve compatibility issues, it could be eventually necessary to abandon conventional materials. Some inherent factors are a problematic co-sintering of metallic interconnects and ceramic cells in SOCs, and 3D printing can open the door for all-ceramic fully printed stacks. Printing incompatibility of metallic bipolar plates and polymeric electrolytes will give rise to develop compatible polymeric-based composite interconnects for PEM.

This expected capability of fabricating new free-shape concepts at different scales (from the μm to the cm scale) have to be complemented with adequate topology optimisation tools not adequately developed at present. The predictive shape method should be able to incorporate multi-physics models, including functional properties, to extend the current use, mainly devoted to improving structural parts to functional devices. It is of particular interest to focus efforts on better modelling the processes taking place at the interface level in PEM and SOCs. This solution is of utmost importance since realistic models will help in generating outputs by simulation that will feed the previously mentioned design optimisation algorithms for design enhancement using artificial intelligence approaches. These studies will yield optimum hierarchically structured interfaces and new device shapes that most likely will require of further improvement of the printing methods, especially of the resolution and the technology hybridisation.

Without any doubt, all these ingredients will give rise to revolutionary PEM and SOC generations of devices that will foster more efficient, durable and compact energy sources for a sustainable future.

Concluding remarks
3D printing of fuel cells and electrolysers, independently on their nature (either ceramic or polymeric), will open a new avenue of possibilities for increasing shape, hierarchical and materials complexity that will solve some of the most relevant issues currently existing, especially at the interface level. Moreover, unexplored geometries driven by topology optimization will increase key performance indicators like specific energy and power while providing them with the required robustness to face new application scenarios, such as the ones in the portable segment. For reaching these goals, it is necessary to (a) dedicate further efforts to completely master the 3D printing of the functional materials involved in these technologies (including the fabrication of high-aspect ratio parts); (b) fully develop multi-material printing required to manufacture full devices in a single printing and (c) successfully couple optimization algorithms to multi-physics phenomena.

Acknowledgments
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3. 3D printing of solar cells

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Status
Solar cell technology is important for ecological sustainability and energy independence. The first commercial solar cells, based on silicon wafer technology, are around for many decades and their technology has shown only incremental progress. Currently, solar energy contributes to a bit more than 2% of the world energy demand (in some countries up to 7%) [18], which clearly indicates that the price per kWh should be further reduced in more locations worldwide to become competitive (with conventional electricity sources) and to obtain significantly higher market shares. Because the efficiency of a solar cell determines its commercial success, this forms the basis of current ongoing solar cell research: increase of photovoltaic efficiency. Research aims at higher efficiencies with cheap materials and novel techniques.

The efficiency of a solar cell has fundamental maximum efficiency using a single p–n junction of 32% for c-Si solar cells. With modern approaches such as tandem cells, the theoretical efficiency is 45%. A strong motivation for fabricating thin film solar cells is the reduction of recombination of electrons and holes and the advantage of lower cost and lower energy consumption during fabrication. The main aim in current thin film solar cell development lays is the improvement of optical absorption by choice of composition and with advanced light management. Promising and challenging aims to fabricate or improve the solar cell by 3D-printing are related to the electric connections, light management and composition/structure of the light absorbing layers. Several parts of the solar cell and the module are also suitable for 3D-printing solutions [1]. For the module, parts of the frame and the sealing are obvious targets for improvement by 3D-printing. In all these directions the fabrication of solar cells or its components is where 3D-printing can have a strong contribution.

Current and future challenges
One of the current challenges of 3D printing is becoming a cornerstone technology for the high-throughput large-scale roll-to-roll fabrication of thin-film photovoltaic (PV) cells on flexible substrates, such as transparent plastics and metallic foils. The most relevant coating and printing techniques in the field of polymer solar cells such as gravure coating knife-over-edge and slot-die are likely to provide opportunities for 3D printing. Moreover, this low (room) temperature fabrication technologies can easily be extended to flexible substrates [20]. In this regard, noncontact inkjet printing, which is a rapid and digital deposition technique with excellent control over the layer formation, has recently been used by Mathies et al [21] to print deposited perovskite layers with a power conversion efficiency of 12.9%. In the work of Andersen et al [22], in-line printing and coating methods have been demonstrated to enable a high yield fabrication of fully roll-to-roll processed polymer tandem solar cell modules.

An alternative to such flexible cells would be based on arrays of interconnected ultra-thin semi-transparent solar microcells, which can reach an efficiency similar to conventional solar panels. This type of solar panel requires flexible front electrodes and current collectors. Ahn et al [23] were able to fabricate flexible, stretchable, and spanning silver micro-electrodes using a three-axis micro-positioning stage coupled to a micro-nozzle (figure 4) showing the potential of 3D printing to support these micro-PV technologies. In the same direction, there is a clear advantage of adapting PV systems to complex geometries. Bernardi et al [24] mounted commercially available Si solar cells onto 3D-printed plastic frames with optimized geometries demonstrating energy densities per projected area (kWh m$^{-2}$) higher than flat stationary panels by a factor between 2 and 20 and an enhancement factor in energy density of 1.5–4 times. Successfully facing the challenge of adapting PVs to optimized surfaces will position 3D Printing as an enabling technology for the next generation of solar cells.

Three-dimensional printing technology can also be employed to improve the photovoltaic and photo-thermal conversion efficiency of modules (beyond the solar cells themselves). In this regard, 3D-printed concentrator has been optically designed and improved for dye-sensitized solar cell modules increasing the photovoltaic efficiency from 5.48% to 7.03% in the work by Huang et al [25]. In the same direction, a combination of a 3D-printed parabolic concentrator and a light cage was also used to demonstrate external light trapping for a thin-film nc-Si:H solar cell with a 15% enhancement of the energy conversion efficiency (figure 5) [26]. Finally, it is also remarkable the recent development light trapping metamaterials and designed surfaces at scales in the order of 200 nm, by using two-photon polymerization (2PP) 3D printing, for light management in various types of solar cells [27]. Overall, one of the challenges and opportunities of 3D Printing is developing high-aspect ratio parts that generally improve the light trapping and management in solar systems.
Advances in science and technology to meet challenges

As mentioned in the previous section, 3D printing of solar cell components opens many opportunities but, to be successful, the process will have to necessarily be competitive with existing manufacturing technologies, address new (niche) markets and be compatible with currently employed materials. In this direction, the main general advances required to meet the challenges are: throughput, speed, accuracy, price, quality, size, fast adaptability, compatibility with existing processes, use of sustainable materials, competitive lifetime of produced solar cells, customization capabilities and protection against degeneration, moisture and oxidation.

Although still pending of full deployment, one of the less complex applications of 3D printing for solar cells are part of the exterior: the module, frame, casing and contacts. These parts often need to be strong and the installation of solar cells often needs custom made frames. A more demanding application will be the deposition of the solar cell active materials and the conductive and protection layers, which can be deposited...
form different of 3D printing solutions, opening up many possibilities. However, some of these materials are very sensitive to oxidation, humidity or degeneration in general, which means that compatible processes based on 3D printers have to be developed. Some options were mentioned before but there is still a lot of work to do in this direction, e.g. capped raw materials, protective atmosphere printing, ultrafast sintering, etc.

3D printing will be likely employed to develop novel concept solar cells where the use of intricate micro/nanostructures, for example light trapping metamaterials and designed surfaces, enhances the light absorption (often in thin film solar cells). Such patterns are already printable with approaches such as 2PP printing but the required time to produce a full solar cell based on this is still very long. Increasing the speed of such low-dimensional patterning is a remaining challenge. A similar approach will provide customized colour and structure to solar cells for fulfilling relevant aesthetic reasons. Beyond printing speed, fully developing 3D printing at large scales will enable industrially feasible light trapping and light concentration structures, which will be fully optimized involving new artificial intelligence design tools.

Concluding remarks
The versatility of solar cells allows a wide range of opportunities for the use of 3D printing in the fabrication and/or development phase. Almost all the parts of a solar cell can be fabricated with 3D printing and it is only a matter of optimizing the process to provide commercial feasibility. It is very important to understand that not only the conventional solar cell modules, that we all know from roofs or solar farms, but also niche markets can play an important role in the development of 3D printing for solar cells. In this regard, reaching a high flexibility in materials choice and mastering the fabrication of nano-, micro- and macro-structures with 3D printing processes will give rise to a new generation of light weight solar cells for mobility, disposable solar cells, solar cells for sensors and actuators (internet of things), solar cells on flexible substrates such as textiles or solar cells for commercial or industrial labelling.

Acknowledgment
N.A.
4. 3D printing for thermoelectrics

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Status
Heat is omnipresent in natural and artificial environments, more than 60% of which is dissipated. Thermoelectric (TE) power generation can provide a unique solution to convert this dissipated, wasted heat into useful energy, that is, electricity (figure 6(a)). Moreover, it is highly convenient that the TE effect is applicable to a wide range of temperatures, from room temperature to ~900 °C, enabling the conversion of low-grade heat such as body heat as well as high-grade heat such as that generated from atomic energy. Generally, TE conversion efficiency depends on the material properties and design of the module structure. However, despite the development of highly efficient TE materials, module engineering is rather less advanced and is still fabricated by the traditional multi-step process of materials synthesis, dicing, and assembly, which restricts the available design of modules to that of planar structures. At this moment, three-dimensional (3D) printing technology can securely maximize the flexibility in the design and fabrication of TE modules into more efficient structures (figure 6(b)). Furthermore, the printing process can significantly reduce the processing cost for the fabrication of TE modules owing to lower energy input and a simplified assembly process. This section reviews the current status and future challenges in the field of 3D printing for the TE power generator (TEG).

In 2018, He et al reported the stereolithographic 3D printing of Bi$_2$Te$_3$-based materials [28]. Since then, significant research effort has been put into developing 3D printing technology for TE materials and modules, expanding the list of printable materials and processes considerably. In addition to the stereolithography process, extrusion-based processes [29], fused deposition modelling [4], selective laser sintering (SLS) [30, 31], and aerosol jet printing [32] have been applied to TE materials such as low-temperature operable Bi$_2$Te$_3$ and BiSbTe, intermediate-temperature operable skutterudites, and high-temperature operable SnSe [33]. Moreover, the 3D-printing process offers an opportunity for new designs of module structures and TE legs such as cylindrical TEGs containing ring-shaped legs [29], 3D conformally printed TE legs [32], and direct laser-sintered TE legs on electrodes [30]. As this field is still in the very early stages of development, there is ample opportunity to enhance the efficiency of 3D-printed TE materials and TEGs.

Current and future challenges
Although the recent developments have significantly advanced 3D printing technology for TE materials, several important issues remain in order to direct this technology into the main paradigm in the TE community, and ultimately to commercialization. From the perspective of material development, most studies reporting the high efficiency of materials still focus on the Bi$_2$Te$_3$-based materials and modules for low-temperature energy harvesting. Bi$_2$Te$_3$-based materials exhibit high efficiency near room temperature; their composition- and structure-dependent properties are well-established, thus providing a good model system to study. However, their operable temperatures are limited to below 200 °C, thus restricting the possible application areas. For example, industrial waste heat at a temperature below 200 °C is not more than 25% of the total, while the application of thermoelectric energy harvesting requires different materials operable at higher temperatures. Such a material limitation originates from the underlying challenge of ink synthesis with desired printability and post-sinterability, which requires precise engineering in the surface and structural properties of materials. These issues are also related to the resulting efficiencies of 3D-printed materials (figure 7). Currently, the reported efficiencies of 3D-printed TE materials are not as high as those of materials synthesized by traditional processes such as hot-pressing, requiring of further enhancement of their material efficiency.

Another important challenge related to the module fabrication by 3D printing is developing elemental technologies to be applicable to printing processes. For example, the module assembly of TE materials involves material metallization and bonding with electrodes, for which printable material has been less explored to date than TE materials themselves. Ag-based inks or pastes are extensively utilized materials as printable electrodes, but these cannot meet the criteria of electrode properties in the typical modules due to the contact resistance with TE materials and possible diffusion of Ag ions. Further, the diffusion barrier layer, such as Ni for Bi$_2$Te$_3$-based materials, should be implemented for the durability of TE modules. The further
development of these elemental technologies will improve the power conversion efficiency in the system and realize the industrialization of TE ink technology.

**Advances in science and technology to meet challenges**

As previously mentioned, to expand the efficient TE materials that are 3D printable, the development of inks with 3D printability and post-sinterability should be first addressed. For example, in the extrusion-based process, the printability of inks depends on their rheological properties, that is, their viscoelasticity, securing flow-like deposition during dispensing, and structural integrity after the deposition. Recent studies of colloid inks containing inorganic particles have suggested that the rheological properties of the inks are strongly related to particle characteristics such as surface charge states, sizes, and size distribution. For example, charged particles are well dispersed in the medium by electrostatic repulsion, which enhances the viscosity of the inks by the enlarged dynamic volumes of the particles as well as the elasticity by the charge interaction among the particles [34]. This particle surface modification can be achieved by using appropriate surface-functionalizing agents, including ionic complexes, surfactants, and polymers. Another important requirement for these agents is that they must not hinder the atomic diffusion path during the sintering of the particles, to secure the post-sinterability. Recently reported composition-matched solders for metal chalcogenides can fulfil these requirements for additives in 3D-printable colloidal inks [35].
Conversely, the improvement of the material efficiencies can be achieved by applying established strategies to bulk TE materials. Nanostructuring has been widely researched in various TE materials to control the electrical and thermal transport by interface scattering engineering, eventually enhancing the material efficiencies [36]. For example, nanostructured BiSbTe bulk materials exhibit increased efficiencies, 40% more than those of microstructured bulk materials. One can easily apply this strategy to 3D-printed TE materials by the integration of nanostructures into 3D-printed TE materials at the ink formulation or sintering stages.

In module fabrication, the recently developed conductive inks containing nano-carbons or metal can provide durability and high performance in the 3D-printable TE modules. Carbon nanotubes or graphene-based inks are widely used as electrode materials for electronic applications and exhibit sufficiently high electrical conductivities to meet the standards of electrodes in TE modules.

Concluding remarks
Considering that the 3D printing of TE materials and modules has been established as the new fabrication route in the TE community, research topics inherent to academia can be suggested based on a review of the history of the evolution in conventional TE technology. The research topics of doping and composition optimization, microstructural engineering, and nanostructuring have been considered in a materials efficiency viewpoint. At least three major fields for further studies can be identified: a deeper understanding of the 3D printing inks and 3D-printed TE materials, 3D module design and fabrication, and system-level applications. The final goal should be to enhance the efficiency and durability in the system. To this end, a close collaboration network between the two different research communities of TE and 3D printing should be established for achieving this purpose. Nevertheless, the issues of cost-effective manufacturing that are often neglected by academia require consideration from a practical point of view, as the greatest potential accomplishment of 3D printing.

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5. 3D printing for batteries

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Status
Storage of energy is crucial in the future society where sustainable energy sources will become dominant. The intermittent nature of energy sources such as wind and solar makes it necessary to improve the energy storage solutions. Battery technology is one of several solutions for storing energy. For large scale energy storage (grid scale) batteries will play a role in short-term storage, up to maybe days, while longer term storage will be solved by other technologies, e.g. synthetic fuels, pumped hydro etc. In the transportation sector batteries will be crucial, possibly in combination with fuel cells. Presently, and in the near future, lithium ion batteries are the dominating technology for electrical cars, and are increasingly used in ferries, trains and smaller trucks. Lithium ion batteries include a number of different chemistries, where especially the positive electrode material varies. Another energy storage technology is the supercapacitors, which has the advantage of very fast charge/discharge rates and long cycle lifetime, but with lower specific energy and energy density. Hybrid supercapacitors have elements from both batteries and supercapacitors and have higher energy density than supercapacitors. Most lithium ion batteries have a fixed format, either cylindrical (e.g. 18650 format) or prismatic batteries and are produced on a large scale. Production of these formats was optimized over a long period with significant focus on consistent and reproducible production. Quality control and homogeneous performance are essential parameters in production of batteries in order to avoid battery degradation and safety issues such as fire.

In many applications it would be an advantage to have more freedom in design, e.g. when constructing devices with integrated batteries, custom-made micro-batteries and batteries for wearables. This is where 3D printing of batteries is of considerable interest as it is possible to design and realize new battery architectures.

Current and future challenges
Early efforts related to 3D structuring were by deposition methods, e.g. using nanorod-patterns. It was only by the development of 3D printing techniques that it became possible to use additive manufacturing to produce 3D electrode structures. A recent example of the possibility of printing customized batteries intended for e.g. integration in drone technology can be found in [37] where a combination of 3D print and aerosol deposition is used for producing customizable, non-planar, integrated lithium-ion batteries.

Development of 3D-printed 3D-structured electrodes has shown a promising route for enhancing the performance of batteries which are then assembled using conventional battery-assembly technology. The battery electrodes (positive and negative) are stacked using a separator membrane or solid polymer electrolyte in such a way that the electrodes are deposited on current collectors and are contacted to the external circuit from opposite sides, as is the case for traditional lithium-ion batteries. The electrodes are in essence patterned 2D electrodes where the improvement in the performance of the batteries is mainly governed by a specific 3D structure of the interface between electrode and electrolyte.

Generally, 3D printed electrode structures can be divided into two classes reflecting the strategy for battery assembly: 3D structuring of two-dimensional electrode surfaces and interdigitated patterns for in situ built three-dimensional electrode/electrolyte structures. Many 3D printing techniques can be used for printing electrodes for batteries, including ink/slurry based methods using dispersions of active materials with different viscosities (inkjet printing, drop-on-demand deposition and slurry extrusion methods) as well as filament printing using e.g. polylactic acid (PLA) based polymer loaded with functional materials.

Advances in science and technology to meet challenges
Yoshima et al [38] published one of the very early reports on depositing a 3D interdigitated anode and cathode pattern in a functional lithium-ion battery [38]. They deposited the electrode structure between sacrificial polymer walls. One of the first real 3D-printed interdigitated lithium ion battery with freestanding electrode structures was reported by Sun et al [37]. The electrodes (LFP: LiFePO4 and ITO: Li4Ti5O12) were printed on pre-deposited interdigitated gold current collector patterns. Figure 8 shows a 3D-printed interdigitated electrode structure using multilayer slurry deposition.
Initially the properties of 3D-printed electrode structures were demonstrated using standard liquid electrolytes. The goal is all-solid state batteries where 3D printing is used also to deposit a solid electrolyte between the two electrodes. As an example, Fu et al. [39] used graphene oxide (GO) containing inks to print interdigitated electrode structures by extrusion-based 3D-printing. The materials used were LFP for the positive and LTO for the negative electrode and the GO gave suitable viscoelastic properties of the slurry for 3D-printing. Subsequent thermal reduction of the electrode structure, where graphene oxide transforms to reduced GO, resulted in very good electronic conductivity of the electrode structure. A polymer composite electrolyte was printed in between the electrodes using a mixture of co-polymer (poly(vinylidenefluoride)-co-hexafluoropropylene, PVDF-co-HFP) and Al₂O₃ nanoparticles to form a solid-state battery [39].

There is a significant research activity on 3D printing of various elements of a battery from interdigitated electrode and solid electrolyte structures to printing the entire batteries. Progress in fully 3D-printed batteries and materials for batteries have been reviewed [1, 40–45], covering energy storage as well as other energy technologies where 3D-printing of functional materials is employed. Overall, in terms of materials, it is necessary to extend the list of printable materials, especially regarding solid electrolytes (either polymeric or ceramic), and ensure suitable processing atmospheres (to deposit moisture- and air-sensitive materials). Development of atmosphere-controlled (industrial) 3D printers and methods are undoubtedly required for this and other fields. Moreover, the combination of several materials in a multi-layer full device requires a deep understanding of the chemical and mechanical compatibility at the different interfaces. Further work is required on this specific topic, even beyond the use of 3D printing (3DP) as a processing technique, looking for stable interfaces presenting good adhesion (even without any applied pressure). In this regard, 3DP can be a relevant tool to reduce chemo-mechanical mismatches arising from volumetric changes during the lithium intercalation mechanism by design. Specific studies on minimization of mechanical stresses based on geometrical or compositional enhanced complexity will be essential.

3D printing of full batteries, including current collection and packaging, has the potential of providing freedom in design and battery format. Moreover, this approach enables the real integration of devices and batteries by combining both in a single manufacturing process, e.g. in drones or wearables (see figure 9) [46]. However, before this represents a real advantage, there are many obstacles regarding optimization, consistency and reproducibility in fabrication in order to achieve the needed goals in battery efficiency, durability and safety. In this direction, the 3D printing and battery communities should agree on a champion combination of materials and methods that ensures reliable battery fabrication while reducing the fabrication cost to competitive values (considering the value-added of customized units). In addition, specific life cycle assessments are required to quantify the environmental impact of 3D printing processes for the battery sector.

Concluding remarks
Using 3D printing methods for battery fabrication is a field where significant progress can be expected in the coming years. The efforts so far include fabrication of various elements in a battery, e.g. 3D printed electrodes, which are used together with a liquid electrolyte, or 3D printed solid electrolyte patterns, which are then assembled using conventional electrode casting methods.

There is little doubt that interdigitated electrode/electrolyte structures will be of importance in future battery development. Interdigitated electrode structures are very efficient in providing short ionic diffusion paths in the solid electrolyte as well as electronic and ionic transport within the electrodes. Advantages
include the possibility of obtaining higher charge/discharge rates and a more efficient packing of the battery structure. Present day interdigitated patterns are basically two-dimensional patterns, which have been extended in the third dimension. A further development into true three-dimensional interdigitated patterns could be one of the next steps in development of 3D-printed batteries. This is a development, which would only be possible to realize using advanced 3D-printing techniques and which would take full advantage of the unique opportunities in 3D-printing.
6. 3D printing of supercapacitors

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Status

Supercapacitors are electrochemical energy storage devices that store energy by the accumulation of mobile ions in a liquid at the surface of a porous electrode under the action of an electric field. Because there are no, or surface-only, chemical reactions at the electrode, charge and discharge processes can be relatively fast and supercapacitor devices can deliver a power of up to 250–400 W kg⁻¹. Because the pulverizing bulk strains of intercalation and insertion reactions—such as those typically experienced by the electrode materials in Li ion batteries—are avoided, device life can be >10⁶ cycles [47]. It is essential that supercapacitor electrodes have high surface area per unit mass and activated carbon (AC) porous micro-particulates (>1000 m² g⁻¹) along with various types of high specific area nanomaterials (for example pseudo-capacitive metal oxides such as MnO₂) are used. The positive and negative electrodes of a supercapacitor can be identical, such as those based on activated carbon, or different, in the case of pseudo-capacitors. Electrodes are fabricated conventionally by continuous coating of an AC-based (or metal oxide) slurry onto a thin metallic foil, large area current collector. Separated by a porous, electrically insulating membrane separator the electrodes are then placed to form the anode and cathode of a cell, and the arrangement of many stacked or wound anode/separator/cathode layers sealed with a liquid electrolyte into mechanically robust, air-tight packaging.

Although manufacture is highly productive, it is characterized by (a) a large amount of work in progress, (b) a large number of discrete assembly steps, and (c) planar electrodes that can only be formed only into simple wound or stacked arrangements.

Current and future challenges

The drivers for the exploration of 3D printing for supercapacitors are (a) to reduce (ideally to unity) the many steps of conventional manufacture, (b) to achieve new, non-planar electrode arrangements that promote more efficient charge/discharge behaviour, and (c) to produce novel device geometries.

The principal challenge to the single-step 3D printing of supercapacitors is to be able to deposit the different components and their constituent materials of a supercapacitor device in a single operation, each with the appropriate spatial control and functional properties. A conceptual approach to single-step manufacture is as follows. First, some part of the housing/packaging should be formed that will provide structural stability, contain the electrolyte, and be chemically inert. Device packages can be readily achieved by 3DP of polymers such as nylon, typically by extrusion free forming (EFF) [48, 49]. Next, a conducting current collector is required, optimally filling as much of the packaging area as possible and usually formed by drying of a conducting ink laid down by ink-jet or syringe deposition; inks usually comprise fine-scale conductive particulates such as Ag, Cu or C suspended in a fugitive suspension. Wetting of the ink onto the packaging is critical and high temperature drying/firing should be avoided.

The first electrode may then be deposited onto the current collector and typically comprises a suspension of active material, a binder to hold the particulates together and to adhere them to the current collector, and carbon black to ensure percolation of current. If a liquid electrolyte is to be used, the printed electrode after drying should be porous. If a solid-state configuration required, the print suspension may additionally include the solid-state electrolyte (e.g. an ion conducting gel) that should be integrated directly into the dense dried electrode as an inter-connected phase capable of percolating charge-carrying ions through the electrode. Electrode deposition is usually from a computer-controlled syringe containing the slurry, via a direct ink write (DIW) device with an accuracy of typically ~10 µm. For higher viscosity slurries (higher solid content), deposition is more akin to extrusion, requires less drying and producing less shrinkage, but fine-scale spatial control is more difficult. Generally, two separate 3D electrodes sub-assemblies are printed (e.g. see figure 10), and then the two electrodes inter-digitated, usually by hand, to form a cell and ideally with no need of a separator because electrodes are prevented from touching by integration into the stiff housing. A liquid electrolyte can then be dispensed into the electrode assembly by a numeric-controlled syringe, usually under a controlled atmosphere. Electrolytes must wet the electrode and the active particulate surface, and be drawn into the pore network by capillarity. Finally, in a fully hands-free operation, further automated printing is required to provide external electrical contacts for operation, and to seal the device package.

Turning to the opportunity for 3D electrode geometries, an example is shown in figure 10 [7] in which a high viscosity electrode suspension (active MXene + Ag nanowires) is directly extruded into a novel electrode pattern, in this case followed by directional cooling to engineer directional pore channels i.e. ice-templatting [50], followed by ice sublimation and back-filling of porosity with an electrolyte. More open,
Figure 10. Schematic illustrating the fabrication process of 3D printed inter-digitated supercapacitor electrodes and the associated steps for high performance [7]. John Wiley & Sons.

Advances in science and technology to meet challenges

First attempts to produce ultimate 3D-printed supercapacitors with novel geometries and entirely fabricated in a single operation are being reported [49]. For example, figure 11 shows a novel ring-shaped supercapacitor printed by combining EFF and DIW. In this case, up to nine different components of the functioning device were deposited to build up the complete unit (figure 11(c)). Moreover, the list of materials includes strongly dissimilar compounds for housing, current collection and electrodes/electrolyte fabrication. Understanding and optimizing the compatibility of materials and printing methods still remains one of the biggest challenges for reaching complete devices (especially at the interface level). Besides, the use of multiple materials involves the development of hybrid printers (including multi-material design and printing software). Mastering multi-material 3DP allows the realization of unexplored architectures and paves the way for future novel configurations. In this particular example, the need for porous separator was avoided by placing electrodes alongside one another but separated by a printed polymer divider ‘over’ which ions transferred in a KOH/polyvinyl alcohol-based hydrogel electrolyte (figures 11(a) and (b)). The electrolyte was accurately dispensed into each concentric cavity containing a printed electrode by a numeric-controlled syringe. Overall, the fully sealed ring capacitor was formed in <30 min and was immediately able to provide a cycling capacity of ∼600 mF cm⁻² at 10 mV s⁻¹, proving the potential of 3DP in the field of supercapacitors.

Overall, the most important challenge is to reach high areal and volumetric capacity at the device scale and comparatively low manufacturing throughput. To overcome this challenge, greater speed and throughput of fabrication is needed, and/or compelling quantified demonstration of energy storage benefits of novel geometric form-factors versus time and cost. Key research issues are bespoke slurry and suspension formulation and accurate deposition technologies for electrodes, separators, electrolytes, current collectors and packaging, and managing adhesion and wetting characteristics to ensure the many dissimilar material interfaces are optimized and long-lasting.

Concluding remarks

Although still relatively unexplored for energy storage devices, advances in 3DP science and technology in other sectors are being rapidly adopted, modified and applied for supercapacitors. The principal opportunities are for novel device geometries and direct, zero sub-assembly, manufacture. A growing
A number of demonstrations are suggesting that the intrinsic supercapacitive properties of materials can be realized in 3DP devices, but overall device-scale performance metrics are yet to compete with conventional formats, which typically lie in the range 5–15 Wh kg\(^{-1}\). Given the maturity, high productivity and relatively low cost of commercial supercapacitors, the near term technological opportunities for 3DP supercapacitors will first be in high value, niche markets where geometrical freedom is valued, such as directly integrated printed micro-supercapacitors, med-tech, and defence markets.

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7. 3D printing of turbomachinery components

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Status
Over the past few decades, the 3D printing industry, also known as the additive manufacturing (AM) industry, has grown steadily, averaging 23.3% growth from 2016 to 2019. AM has found its way into nearly every industrial sector, including the manufacturing of turbomachinery components [56].

In the turbomachinery sector, AM processes capable of producing metallic parts are required. Laser beam direct energy deposition (DED-LB) as well as laser beam powder bed fusion (PBF-LB), are well known for their suitability to produce layer wise parts designed in 3D computer-aided design (CAD) [57].

Both technologies are already used in manufacturing and/or repair of various turbomachinery components. Prominent examples are the repair of individual damages that occur on turbine blades after being in service, the hybrid production of components (see figure 12) or the flexible production and further optimization of customized parts with highly complex geometries [57–62]. In this context, it is crucial that the strengths of the respective technology are used correctly: While DED-LB manufactured structures can be applied directly onto 3D surfaces, PBF-LB manufacturing offers higher detail resolution and freedom of design, but the part must be built on flat surfaces and is supported by a powder bed.

Through the transition from subtractive to additive manufacturing in conjunction with the possibilities of new lightweight designs, and a flexible production adapted to the needs, AM opens up opportunities for resource conservation and sustainability through savings of material and energy thus reducing waste in production [63].

However, AM in the turbomachinery sector faces several big challenges, including high costs per part compared to conventional manufacturing methods, a limited material range that exclude crucial turbomachinery alloys and a limited transferability of results between machines.

Therefore, current research projects are concerned with the development of tailor-made materials to improve AM-material properties, or with accelerating the process to increase build-up rates. The use of sensors for process monitoring and the integration of simulation methods and artificial intelligence (AI) promises to improve process stability and thus reproducibility and to enable quality assurance. Further development of the digital process chain over the entire life cycle is also conceivable to make the production processes more efficient [63].

Current and future challenges
To establish AM as a sustainable, industrial scaled method in the turbomachinery sector, not only technological but also organizational challenges must be solved (figure 13).

On the technological side the most important challenges are an increased productivity and thus lower cost per part as well as an improved quality control. Both challenges are particularly driven by AM users, not only in the sector of turbomachinery but in general and are subject of many current research projects.

A more prospective technological challenge is the limitation of manufacturable materials for AM. Many common materials for turbomachinery applications (e.g. nickel base superalloys) are especially designed for conventional manufacturing routes like casting or forging and are classified as hard-to-weld. AM of these materials often requires special process conditions, like elevated temperatures, or it is simply not possible to manufacture them without defects like microcracks. In the latter case costly post processing (e.g. hot isostatic pressing) must be applied to generate a defect free part [64].

One of the key organizational challenges for AM in the field of turbomachinery is to integrate AM as a possible method for production-ready design. The new geometrical freedom enabled by an AM method raises depth of production and shifts the perspective from a single process step to a complete process chain. The gained flexibility due to increased freedom of manufacturing comes up with a higher complexity to handle the AM processes to meet requirements. Challenges in handling AM processes come next to a need of evaluation: closed quality control chains for additively manufactured parts, including defect detection during the process and online adjusting of process parameters to avoid these defects, a detailed characterization of digital materials (e.g. lattice structures as material properties) and the full integration of the AM process into digital process chains, needs to be approached.

Finally, facing these challenges and seeing AM as a driver for innovations, current and future engineers need to know how and when they can use AM for their products and which potentials can be raised when doing so. Therefore, international standards and rules must be extended or even totally new defined.
Advances in science and technology to meet challenges

To successfully solve the current and future challenges of AM in the field of turbomachinery, it is necessary to take a holistic view of the AM process chain on an industrial level.

Dealing with technological challenges is part of the vertical process chain and includes further development of machine concepts and process adaption. Saleable multi-laser PBF-LB machines or the extreme high-speed laser application (EHLA) material deposition to manufacture three dimensional parts (EHLA 3D) are examples of these recent developments targeting higher productivity and are already partly proven for the use in turbomachinery applications. Further approaches are hybrid AM processes, where AM structures are combined with conventional manufactured preforms to enable faster cycle times.

To lift the manufacturing limitations for conventional high temperature (HT) materials, preheating concepts for direct heating of the melt pool area are currently in a state of validation. On the edge of the vertical process chain the investigation of the unique process characteristics of AM such as high cooling rates and small melt pools, bear a chance to develop tailored AM-materials. Especially oxide dispersion strengthening nickel-based materials seem promising in achieving HT properties comparable to leading HT materials currently in use [65].

Online process monitoring systems form the link to the digital process chain and in combination with automated or AI supported analysis methods are crucial modules for enhanced quality control to finally fulfil
the high-quality standards in the turbomachinery sector. Concrete examples are the online adjustment of process parameters to avoid errors during the process and the automatic geometry acquisition.

The integration of the digital data into the horizontal process chain can be used as a tool to manage handling AM parts in pre- and postprocessing steps. Data from the automated geometry acquisitions during the AM process serve as baseline for the post grinding process, to simplify path planning, predict geometric and surface quality and thus lead to a more efficient process with less quality scatters. The combined data along the process chain can be included via cloud computing and AI into future computer-aided design and computer-aided manufacturing systems (CAD/CAM-systems) to reduce their complexity and enhance process design for complex AM manufactured parts.

**Concluding remarks**

Consistently addressing the existing challenges of AM in the turbomachinery sector by taking a holistic view of the process chain leads AM to a full fledge manufacturing method which offers a significant expanded degree of freedom in design and in development. With this expansion in the production AM is key part of the development of a new generation of more efficient and greener turbomachines to meet the future challenges of the energy sector.

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8. 3D printing for chemical reactors

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Status
Conventional flow-through reactors for heterogeneous catalysis such as packed beds or monoliths suffer from flow mal-distribution, hotspot formation, a high pressure drop, or limited mass and heat transfer. An attractive alternative to overcome these issues is the use of millimeter-scale flow reactors with micro-structured internals [66]. Additive manufacturing (AM) allows a design freedom and flexibility that cannot be achieved through conventional fabrication processes, thus enabling reactor designs tailored to a specific application. Optimized continuous flow reactors offer significantly enhanced mass and heat transfer, thereby improving the efficiency and safety of the process. Indicatively, the mass and heat transfer characteristics of 3D printed internals, based on the associated Sherwood (Sh) and Nusselt (Nu) numbers, are depicted in figure 14(a) and compared to conventional reactors. In addition, the catalyst distribution within the reactor can be optimized, and coupling computational fluid dynamics (CFD) with kinetic models can provide additional insights, specifically regarding local temperatures and concentrations, thus providing further handles for performance optimization [6]. Figure 14(b) qualitatively depicts the conversion along the axial direction of the reactor for a first-order exothermic reaction for the cases of a uniform and an axially increasing catalyst loading. The total catalyst loading in both cases is identical, only the distribution changes. A lower catalyst loading near the inlet results in a lower conversion gradient and reduces the hotspots near the inlet. Nevertheless, the increasing axial catalyst loading results in a higher conversion at the reactor outlet compared to the uniform loading case. Through the combination of 3D printing and modelling tools, reactor internals will become feasible that optimize both geometry and catalyst distribution; for conventional manufacturing and deposition processes, such a degree of optimization is out of reach.

Current and future challenges
Each 3D printing method has limitations regarding materials, possible geometries, dimensional accuracy, and spatial resolution. For instance, extrusion-based multi-material printing cannot meet the need for mixing different materials in arbitrary ratios (e.g. to realize non-uniform catalyst distributions). Multi-material dynamic light processing by successively changing vats is impractical and suffers from a limited selection of materials with generally poor chemical resistance and residual monomers [6, 70].

A major challenge lies in the immobilization of the catalyst in a well-engineered approach. Catalyst deposition via additive manufacturing is typically done by integrating the catalyst in the build material or through a separate functionalization step after 3D printing. It is difficult to obtain a printable catalyst composition that has a high enough catalyst content while remaining in the optimal parameter window for printing (rheology, light transmission, …). Furthermore, for vat- and powder-bed printing methods, it can be a challenge to remove unwanted build material from structures with small pores, resulting in pore blockage. Efficient use of materials is another point of attention, since most approaches are not able to fully use a build material, which can be costly when using expensive catalysts (e.g. precious metals).

A particular challenge is the fabrication of supported metal catalysts (e.g. metal nanoparticles) through simultaneously printing with the support (e.g. a ceramic powder). In this case, post-processing can be detrimental when the support material requires high-temperature sintering (e.g. to achieve sufficient mechanical strength) because of the inevitable growth of the catalyst particles and the resulting lower catalytic performance. Similar challenges related to post-processing appear when using 3D printing to shape heterogeneous catalyst powders with a thermally labile component. In some cases, sintering can be bypassed through the selection of a binding method that results in unsintered parts with sufficient mechanical strength and chemical resistance under reaction conditions. Since the binder remains present in this approach, it must be ensured that it does not block the active sites or pores of the catalysts.

Advances in science and technology to meet challenges
The development of additive fabrication as well as modelling tools will impact the above mentioned challenges of chemical reactors development. Improvements in 3D printing resolution and accuracy will enable the fabrication of smooth surfaces and better control over the micro/mesoporosity of catalytic structures. For instance, recently, XJet launched the Carmel 1400C high-resolution inkjet ceramic printer that forms 3D parts with high levels of accuracy, detail and surface finish. The 3D printer has a DPI resolution in the range of 1300–1500 and spatial x-, y-, and z-resolutions of around 20 μm [71]. A desired next step towards sophisticated 3D printed catalysts and reactors is the one-step printing of reactor internals with an optimized catalyst distribution. High-resolution inkjet printing is one of the most prominent
Figure 14. (a) Nu and Sh numbers of 3D printed internals and conventional heterogeneous reactors calculated from \[66-69\] and heat/mass transfer correlation \[\text{Nu} = \left( \frac{\text{Pr}}{\text{Sc}} \right)^{1/3},\] with Pr and Sc corresponding to the Prandtl and Schmidt numbers, respectively. Representative CAD designs of the corresponding structures are depicted on the right of the graph. (b) Conversion profiles along the reactor length for reactors with a uniform and an increasing catalyst loading in the axial direction. The total catalyst loading is the same for both cases. The 3D representation of the reactor internal is cut diagonally for illustrative purposes.

multi-material 3D printing techniques and benefits from a broad material selection. The picoliter droplets deposited during inkjet printing result in thin catalytic coatings that prevent the diffusion limitations (e.g. encountered in much thicker wash-coats). Moreover, catalyst libraries can be screened rapidly by printing multiple catalytic inks simultaneously in different ratios \[72\]. Using this approach in 3D printing, catalysts can be deposited at the desired location within the 3D structure by printing support material (or binder) and active particles using separate printheads. Secondly, the local catalyst concentration can be controlled through the spacing of the inkjetted droplets, or even on a finer level by 'grayscale printing', in which the droplet size is varied \[73\]. If required, the local catalyst concentration can be further controlled by several passes of the printhead over the same position.

Advances in modelling tools will also play an essential role in the fabrication of optimized catalytic reactors. Coupling CFD with detailed microkinetic models capturing the processes on the catalytic surface increases complexity, computational time and resources \[6\]. While kinetic models and mechanisms have been widely studied and organized in libraries for bulk industrial processes like steam cracking, other types of reactions have not been investigated extensively. For example, OpenSmoke++ can handle simulations of combustion processes of hydrocarbons that can be easily incorporated into multi-dimensional CFD codes at a reasonable computational time \[74\]. Extending kinetic models' library as well as the communication network between open-source solvers could motivate researchers to expand the range of reactions in continuous flow reactors.

Concluding remarks
Hand-in-hand evolution of additive manufacturing with multiscale modelling tools and experimental evaluation of the resulting complex chemical reactors internals will lead to an unprecedented level of optimization of flow reactors. 3D printing enables precise control over geometry, with high accuracy and flexibility, but the field still faces substantial challenges to resolve the practical challenges in heterogeneous catalysis and reactor engineering. An interdisciplinary approach and open communication between scientists and engineers with different expertise is essential for designing, optimizing, and implementing innovative flow reactors.

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9. 3D printing for solid-state refrigeration

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Status
Solid-state refrigeration based on caloric effects is a new and promising alternative technology to existing vapour compression cycles due to its potential for high efficiency, environmental friendliness, lower noise, safety, and ease of integration [75]. To reach the requirements for industrial applications, new processes to improve the system designs, efficiency, and performance need to be developed. Here, 3D printing provides flexibility in the materials that can be used, including metals, ceramics and polymers, simple processing and no material waste. Solid-state refrigeration is based on reversible temperature changes of a material in response to externally applied fields, so-called caloric effects. The applied field can be a magnetic field for the magnetocaloric effect (MCE), an electric field for the electrocaloric effect (ECE), uniaxial strain for the elastocaloric effect (eCE) or isostatic pressure for the barocaloric effect (BCE). A cooling cycle of such solid-state refrigeration is analogous to that of vapour compression, as shown in figure 15. The current research on caloric effects was triggered by the observed ‘giant’ values of eCE, MCE and ECE in the 1980s, 1990s and subsequent 2000s [75, 76]. Realizing the promising capability of caloric systems will require high-performance caloric materials shaped in efficient heat transfer structures. 3D printing provides the capability of creating complex internal geometries and implementing a variety of different materials suitable for caloric technologies.

Current and future challenges
Although each caloric cooling technology has unique challenges, they all require a solid refrigerant with a large caloric effect and effective heat transfer between the solid refrigerant and thermal reservoirs. The major challenges to 3D printing of high-performance caloric devices are: (a) To find materials that retain their properties through the 3D printing process, (b) Identifying and realising efficient heat transfer structures, and (c) Producing structures that are fine enough to achieve high heat transfer performance while withstanding the stresses of the particular applied field for many cycles.

Advances in Science and technology to meet challenges
Materials design
In order to obtain a large caloric effect over a wide temperature span, coexistence of different caloric phases may be realized through compositional tuning or addition of nanocomposites. By employing 3D printing, the performance of single-phase caloric materials or nanocomposites could be further enhanced by optimizing the size and geometry [77], the homogeneity of materials, the shape, concentration and orientation of fillers and even by creating texture and cascaded units. Beside for the caloric aspects, other structural issues related to the driving field and heat transfer should be considered concurrently. For example, optimized geometries of magnets used in MCE and mechanical loading components in eCE and BCE should also be considered as target applications using 3D printing [78]. In addition to a single caloric effect, larger thermal changes may be obtained for multicaloric systems in response to more than one type of driving field applied simultaneously. Similar to revolutions made in multiferroic materials, multicaloric materials may be realized by composite configurations [79]. Cooperative effects between different caloric materials in a composite may be gained further advances by 3D printing. Any post processing of the 3D printed components, i.e. heat treatment, is also important and should be optimized to improve the final caloric properties of the device.

Efficient heat transfer structures
Active caloric regenerator (ACR) consists of a porous, solid matrix of caloric materials and are employed in the majority of caloric devices. For example, in magnetocalorics the ACR is often comprised of spherical particles, irregular particles or parallel-plates. However, the former lead to reduced efficiency due to a high pressure drop while the later require very thin plates with small and highly accurate plate spacing. The potential of 3D printing is the ability to fabricate ACRs with complex geometries, a high surface-to-volume ratio and optimized hydraulic designs. These cannot be constructed using traditional material processing due to the limited machinability and brittleness of the magnetocaloric materials. An example of complex
shapes made by selective laser melting \[80\] such as a wavy-channel block and an array of fin-shaped rods are given in figures 16(a) and (b). As seen in this figure, the surface quality of the flow channels is not well defined and far from being ideal. This example illustrate that the quality of these channels, i.e. the transfer of heat, should be improved to enhance the caloric performance \[81\]. Other examples illustrate that thermal switches or diodes are another promising solutions to achieve solid-state refrigeration without moving parts, this open up the possibilities of applying multi-material using 3D printing \[82\].

Fine structure for a long-term cycling

Stable and long-term cycling of materials is currently hindered by hysteresis, electric losses (Joule heating, eddy currents), cyclic stability, and fatigue. For example, electrocaloric materials should be able to operate under a large electric field with specific frequency without breakdown for a life expectancy about 10^9 cycles. A multilayer capacitor structure is a possible solution, and it will be advantageous if the electrodes and active ceramic materials could be fabricated in the same 3D printing process. Hysteresis associated with phase and structural transitions is detrimental to energy efficiency and cycle durability. For eCE cooling, the hysteresis, as well as the loading mode (tension or compression) and frequency, impact the fatigue of eCE components and consequently govern the lifetime of the device. Disordered systems, namely spin glasses, relaxor ferroelectrics and strain glasses will effectively suppress the hysteresis and broaden the working temperature span of the device. As shown in figures 16(c)–(k), fatigue-resistance with considerable improvement in elastocaloric efficiency was achieved through hysteresis minimization in a nanocomposite \[83\]. In addition to gaining feedback from experiments, topology optimization will be an efficient route to predict and design caloric structures both in terms of the heat transfer and distribution of applied field \[84\].

Concluding remarks

Solid-state cooling technologies based on caloric effects are promising but more progress is required before real commercial products are available. 3D printing is a versatile and flexible process technology that is expected to lead to progress in caloric systems. This will allow increasing stability and improving heat transfer in devices. 3D printing of materials for solid-state refrigeration is at an initial stage, and progress in the development of new and advanced 3D printing technologies and better predictable theoretical models which are expected over the next years will push this area towards a better and sustainable society.

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**Figure 15.** Schematic of a solid-state cooling cycle utilizing caloric effects. There are four caloric effects, namely the magnetocaloric effect (MCE), electrocaloric effect (ECE), elastocaloric effect (ECE) and barocaloric effect (BCE) caused by a change in the magnetic field, electric field, stress or pressure, respectively. During the caloric cooling cycles, external magnetic (H), electric (E), stress (σ) or pressure (P) fields are utilized to reversibly change the order parameters magnetization (M), polarization (P), strain (ε) or pressure (P) respectively, to generate an isothermal entropy change or adiabatic temperature change (ATC).
Figure 16. (a) Magnified view of channels made by SLM with LaFe11.7Co1.3Si. (b) Block with wavy-channel geometry. Reprinted from [80], with the permission of AIP Publishing. (c) Schematic representation of a powder-feed laser-directed-energy deposition process. (d)–(i) Photographs of produced Ni–Ti nanocomposite rods, tubes, and honeycombs, respectively. SEM image (j) and bright-field TEM image (k) of as-built Ni51.5Ti48.5/Ni3Ti nanocomposite. From [83]. Reprinted with permission from AAAS.

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10. Additive manufacturing for CO₂ capture technologies and other separation processes

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Status
Solvent-based absorption is currently considered the most matured post-combustion carbon capture (CC) technology, which is reflected in the high number of carbon dioxide (CO₂) absorption research projects with a high technology readiness level compared with membrane separation, adsorption, cryogenic distillation, or other processes [85]. However, significant drawbacks prevent CC from attaining commercial viability, including high corrosion rates and low CO₂ capacity, and the biggest challenge is the high energy penalty associated with any CC process. Estimates place the energy cost of amine absorption at 3.7 GJ tonne⁻¹ CO₂ [86]. In recent years, much attention has been devoted to developing process intensification technologies that can reduce the effect of the drawbacks associated with CO₂ absorption [87].

One energy-reducing process modification that has attracted significant attention is interstage cooling, which involves ex situ cooling of the solvent by separating the absorber into stages, with an external heat exchanger in between. The solvent is drawn off and passed through the heat exchanger to be cooled before being returned to the absorber. The motivation behind this approach is to control the accumulation of heat that occurs in the absorber due to the exothermic reaction between CO₂ and the solvent. The resulting temperature bulge created by the reaction heat has deleterious effects on the reaction. At higher temperatures, the reaction equilibrium tips toward desorption [88]. Furthermore, the CO₂ solubility in the solvent decreases, which reduces the driving force for absorption [89]. Venting excess heat from the reaction and maintaining the absorber near the optimal temperature of 40 °C is expected to improve the capture efficiency, enabling equal capture performance to be achieved at lower energy consumption.

Efficacy of CO₂ absorption processes is strongly affected by heat and mass transfer phenomena, which directly depend on the geometry of reactors and heat exchangers. In this regard, additive manufacturing has greatly expanded the range of geometries and topologies available to designers. Moreover, this newfound design freedom is commonly employed to reduce part count and complexity [90], which is essential for application to interstage cooling, where the associated challenges are a direct result of undesirable process complexity.

Current and future challenges
Most information on the efficacy of absorber interstage cooling has come from process simulations. Those studies have generally predicted significant improvement in reboiler duty and CO₂ capture efficiency. Although experimental data are limited, pilot plant studies employing intercooling have demonstrated improvements in line with simulation predictions [91]. The challenges with interstage cooling are the increases in plant complexity and process footprint, which are associated with additional capital costs. Cousins et al analysed 15 flow sheet modifications for absorption and found that interstage temperature control increased the number of unit operations by 10, the most for all the process modifications they investigated, as well as the number of controls (additional flow, pressure, and temperature controllers necessary) by 8 [92]. Furthermore, this setup interrupts solvent flow by diverting it to an external heat exchanger. While the solvent is outside of the absorber, no mass transfer occurs. These drawbacks inhibit the benefits that can be derived from interstage cooling. Reducing the number of unit operations and controls necessary for operation by better integrating the technology into the absorber could significantly enhance its performance. In this regard, employing additive manufacturing, the number of units can be reduced, and the diverting of solvent flow avoided, by switching to in situ heat exchange (i.e. by integrating heat exchange into the same space where mass transfer occurs, thereby creating a multifunctional interstage heat-exchanger reactor).

Through additive manufacturing, this multifunctional reactor can be achieved in a novel way by embedding heat exchange channels inside the walls of the structured packing conventionally employed in absorbers. This concept results in a monolithic device that is functionally identical to conventional structured packing on the outside but capable of exchanging heat with fluid flowing on the inside. A prototype for such a device, dubbed the 'intensified packing device,' is shown in figure 17 (as designed, manufactured, and tested at the US Department of Energy’s Oak Ridge National Laboratory, ORNL). The device is composed of double-walled packing sheets, which allow cooling fluid to flow in the space created by the double walls. Manufacturing of the intensified packing device involves creating a profile of the packing cross-section and extruding a segment of the packing at a fixed angle, patterning into two parallel panels with gap for fluid and mirroring and rotating the adjacent panels, patterning into a full packing and cutting
into a cylinder, creating a manifold for coolant to flow and adding inlet and outlet ports, and finally manufacturing from CAD to part. Overall, specific features of this particular device illustrate design advantages of 3D printing for intensification of chemical processes like CO$_2$ conversion, e.g. the monolithic nature of the final reactors, the possibility to embed complex fluidics (channels, manifolds, double-walled plates, etc) or the increase of the surface area by corrugation/patterning.

Pressure drop at geometries with increased complexity like the ones reached by 3D printing represents a potential issue to be considered. In the previous example, the pressure drop at the absorber was a significant concern. However, hydrodynamic testing demonstrated that the device only has a moderately higher pressure drop than a conventional structured packing geometry [9].

The benefits of using a 3D printing approach for fabricating complex CC systems are difficult to quantify in general terms. In the particular case presented above, the performance enhancement was substantial. The device improved CC efficiency using monoethanolamine solvent by as much as 15%, which exceeds the best predictions for a conventional interstage cooling process (figure 18). The heat transfer coefficient of the intensified packing device was calculated to be in the range of 89–150 W (m$^2$K)$^{-1}$, which lags behind the heat transfer performance of conventional heat exchanger designs [93] because of the three-phase system. The magnitude of the improvement and the heat transfer coefficient heavily depended on gas flow rate. A detailed heat transfer analysis revealed that the limiting heat transfer resistance is between the solvent and
surface of the packing, which suggests that reducing this resistance would produce the most effective improvements of heat transfer performance.

**Advances in science and technology to meet challenges**

Bench-scale studies already showed first successful proof of concept for an additively manufactured monolithic heat exchanger-reactor. Although the enhancement of CC was proved, the intensified packing device can be further improved by enhancing its heat transfer performance. A higher heat transfer coefficient can be achieved by increasing the solvent wettability of the external surface of the device’s corrugated plates. Moreover, further improvement is possible if higher surface areas are implemented. An increase of the active surface is possible increasing the hierarchical complexity of the system, i.e. fabricating tunable features at different scales. This multi-scale printing still remains a big challenge, especially at the microscale, but great benefits would be expected.

Because design of CC systems is still in its first iterations, the full potential of the technology has not been fully realized. As mentioned, the design freedom offered by additive manufacturing is unprecedented. The initial geometry for the intensified packing device is still based on conventional structured packing element, but without the constraints imposed by conventional manufacturing, new and complex geometries can be implemented. Topology optimization on the intensified packing device will have to be performed to determine its full potential.

Overall, intensified packing device concepts demonstrate the important role that additive manufacturing can play in process intensification of chemical processes, and especially in separation processes such as CO₂ capture from flue gas. This concept is complementary to the advanced manufacturing concept for electrosynthesis of fuels and chemicals from CO₂ that has recently been discussed in the literature [94]. Additively manufactured structured packing devices for columns that can also work as heat exchangers can be used in absorption and in distillation columns, where thermal management is critical for optimal separation. Advanced manufacturing provides design flexibility and multifunctionality, which are key to process intensification.

**Concluding remarks**

Advanced manufacturing is particularly suitable of the fabrication of intensified packing devices for CO₂ absorption from flue gas, which is an exothermic reversible reaction. For cases in which the concentration of CO₂ increases from fuel properties or the heat capacity of the solvent decreases, the role of the intensified packing device in the CO₂ capture efficiency will be even more important. Such cases are applications in which biomass combustion and nonaqueous solvents are used to combine bioenergy with CC and storage to directly reduce the atmospheric CO₂ concentration. In such applications, the solvent temperature will increase more rapidly in the column, and in situ cooling by the intensified packing device would be most beneficial. Beyond CC applications, advanced manufacturing can similarly be employed to manufacture intensified devices for other chemical processes, such as distillation, where thermal management is also critical.

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11. 3D printing for cooling of electronics

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Status
Thermal management in electronic packaging of power electronics, telecommunication systems, data centres and portable devices is challenged by a sustained increase in cooling demand and compactness. This has led the thermal management community on a search for novel cooling solutions, which ultimately accommodate higher heat dissipation with minimum operational costs such as from pumping power. Junction temperatures must be maintained below design limits to avoid degradations in performance, reliability and lifetime. The broad spectrum of electronic devices contains passive and active cooling technologies, ranging from conventional air cooling to liquid cooling and two-phase systems. Air cooling is the conventional heat removal technique and a persistent technology. For higher power dissipation devices (e.g. high-performance computing and power electronics) liquid cooling is already being adopted [95, 96]. Passive two-phase cooling systems such as heat pipes have gained much attention for cooling computer processors, but are inadequate for future cooling requirements [96]. Active two-phase cooling systems remains an active research area for high power density applications, however, market penetration is still pending.

Additive manufacturing (AM), commonly known as 3D printing, offers a distinct potential from the ability to manufacture hyper-complex geometries. This allows for the manufacturing of extraordinary 3D heat sinks for cooling electronics with enhanced conjugate heat transfer and fluid dynamics that are otherwise impossible to manufacture with conventional manufacturing methods. Most research in this area has dealt with air-cooled heat sinks, typically natural convection or forced convection, taking advantage of creating novel intricate fin shapes with rougher surfaces [97]. While current heat sink designs rely on human perception, simulation, testing and rethinking with the constraints of conventional subtractive manufacturing, computational optimization for tomorrows designs are gaining increased attention with the advances in AM processes. For example, Dede et al [98] employed topology optimization and AM to develop and fabricate an air-cooled heat sink and demonstrated considerable improvements compared with conventional manufactured pin fin designs (CAD model represented in figure 19). AM for electronics cooling is still in its infancy and yet a rapidly evolving technology. It has already demonstrated the ability to produce viable devices for cooling electronics [97].

Current and future challenges
Materials, porosity and derived limitations in thermal conductivity is an important challenge for the adoption of AM heat sinks for electronics cooling. A post-heating treatment can leverage the thermal conductivity of common AM metals such as aluminium alloys (e.g. AlSi10Mg and Al 6061) and copper alloys (e.g. CuNi2SiCr) and reach up to 190 W mK$^{-1}$, which is close to pure aluminium. This is yet half that of common copper alloys used for conventional subtractive manufacturing and highlights a considerable shortage. Similarly, the thermal conductivity of polymers may be increased by particle reinforcement (polymer composites) although the current low values (<10 W mK$^{-1}$) limit their application to low heat dissipation devices.

Minimum feature size versus the build volume is another challenge. Electrochemical fabrication, a group of processes based on photolithography and electrodeposition of metals, may fabricate minimum features around (4–25) μm with 2 μm tolerances, but supports only a limited set of materials and small build volumes [99]. On the other hand, SLS processes are less expensive and may fabricate minimum features around (200–400) μm with 50 μm tolerances [99]. A high surface area to volume ratio is essential for improved forced convection heat transfer in confined spaces. This implies that the structural features become as thin as possible while keeping the structural strength. Shorter fluid flow lengths are further necessary for keeping a minimum pressure drop penalty.

The miniaturization and power densification in future microprocessors and wide-band-gap power electronics are ever-increasing and their performance is ultimately reliant upon indispensable advances in cooling technologies. High heat flux two-phase cooling systems are progressively being investigated academically for improved boiling performance through means of micro- and nanoporous surfaces, grooves and channels [100, 101]. A common effort is to increase the surface area in contact with the evaporating fluid, increase the number of active nucleation cavities and improve the liquid wetting of the surface while avoiding flow instabilities and critical heat flux. The latter is characterized by a sudden temperature excursion due to surface dry-out and eventual electronic device failure. Compact heat pipes are challenged by
the thickness limitations in portable devices such as mobile phones and much thinner vapour chamber technologies promise to place these solutions closer to the heat source [95].

**Advances in science and technology to meet challenges**

Advances in AM technology may extend the heat removal rate of electronic cooling systems to meet future power densification. As AM processes and technologies continue to evolve, new materials and post-processing techniques are expected to develop for high thermal conductivity metallic and polymer composite prints. Recent research on polymer composites and 2D materials such as graphene and boron nitride has shown the potential to preferably align the orientation of particles by finely controlled printing parameters, improving through-plane thermal conductivity [102].

Minimum feature sizes and tolerances are expected to decrease while build volume and build rate increase as the technology matures. This will increase the competitiveness of the technology and decrease the cost of adoption correspondingly [56].

Future developments are expected for controlling progressively local properties such as surface roughness, porosity and hermeticity. This encompasses a scalable in-situ approach, in which dense structures co-exist with microporous features or surfaces, such as the novelty demonstrated for liquid electronics cooling by Collins *et al* [99, 103]. In a collaborative effort with the AM vendor, investigating laser and scanning parameters, these authors created a manifold microchannel and a permeable membrane microchannel (PMMC) with a porosity of 17%. These prints are represented in figure 20. Taking advantage of the tortuous flow conditions in the porous wavy membrane, having a high surface area to volume ratio and strong fluid mixing, the PMMC resulted in the highest heat transfer performance at even lower pumping
power. Similar advantages in local property controllability could be revealed for high heat flux two-phase systems, in which dense microchannels with enhanced microporous surfaces could be developed as well as intricate and separate liquid supply and vapour release manifolds that could further improve boiling performance and flow stability. Advances in porous controllability may further promote the development of AM heat spreaders such as two-phase heat pipes and vapour chambers, in which capillary action in porous wicks force the liquid flow to the evaporator.

Concluding remarks
Additive manufacturing provides a 3D playground for thermal engineers and researchers to optimize conjugate heat transfer problems that are pertinent to electronics cooling. Porosity and surface roughness are seldom desired outcomes of certain AM processes. Conversely, these parameters can be capitalized upon for heat transfer enhancement. Combining AM with computational techniques such as topology optimization [104] represents a promising approach for tomorrow’s creation of extraordinary heat sinks.

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Data availability statement
No new data were created or analysed in this study.

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