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An Investigation of 3D Printed Parts Specifications and Applications in Catalytic Substrates and Fuel Cells

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Article Information

Article Type:
Research Article

Article History:

Received: 30 March 2023
Received in revised form
29 May 2023
Accepted: 19 June 2023
Published on line 20 June
2023

Keywords

Digital Fabrication
3D Catalyst Substrate
Directional Porosity
Additive Manufacturing
3D flow pattern

Abstract

Along with simulation and data processing tools, computer-aided manufacturing technologies have changed the design and manufacturing methods of functional parts. The emerging field of fuel cells and catalytic technology in chemical engineering is also of great interest. In addition to expanding the capabilities of 3D printing, the transfer of digital data and physical parts in computer-aided manufacturing methods will benefit research into reactors, structured catalyst design, and micro fuel cells. Additive manufacturing combines theory and experiment by enabling the design of optimized geometries using computational fluid dynamics. Considering computational modeling and 3D printing as digital tools, this article addresses the design and construction of new structured reactors and fuel cells and also explores the fabrication of micro and solid oxide fuel cells using Additive Manufacturing (AM) and Digital Light Processing (DLP). To do so, samples of a structural catalyst substrate with the unique property of changing surface parameters and six different geometries for plates with the optimal flow in fuel cells were 3D printed, and the results of initial tests confirmed the advantages of this manufacturing method. In this article, we discuss how digital fabrication and computational modeling are intertwined in the field of manufacturing engineering, materials science, and chemistry.

Cite this article: Jabbari, A., Khajehhaghverdi, A. (2023). An Investigation of 3D Printed Parts Specifications and Applications in Catalytic Substrates and Fuel Cells. DOI:10.22104/HFE.2023.6051.1257

Publisher:Iranian Research Organization for Science and Technology(IROST)
DOI:10.22104/HFE.2023.6051.1257

1. Introduction

The fourth industrial revolution has led to a fundamental change in many areas, from manufacturing to communications and consumer goods to health issues and everyday applications. Computer-aided manufacturing technologies have revolutionized the way functional parts are manufactured and customized with updated simulation approaches and data processing capabilities. An integral part of digital manufacturing methods is the transfer of information between the computer model and its physical embodiment as quickly and seamlessly as possible. Unlike traditional manufacturing processes, digital techniques offer considerable flexibility, and unique parts tailored to specific performance can be produced more efficiently [1]. Materials, layering techniques, and the way in which layers are connected are among the most noticeable differences among commercialized 3D printing technologies. In the 3D printing process, complete and very complex parts can be produced by superimposing two-dimensional layers. Of course, in each case, there is a balance between layer thickness, surface finish, and printing time [2]. Choosing thinner printing layers usually improves surface quality but significantly increments the printing time and cost. Figure 1 shows the schematic process of preparing to produce a part using 3D printing or additive manufacturing. Regarding the mechanical properties of the manufactured parts, comparisons of the reproducibility between conventional manufacturing technologies and the digital model have been discussed in many studies [3], [4 However, in fields such as chemical engineering, the use of optimized computational geometries has received very little attention. Interestingly, the optimal geometry of reactors gives the designer many ways to control temperature uniformity and fluid dynamics. In addition, the properties of 3D printed materials are often discussed in terms of mechanical properties, and their chemical performance and catalytic activity have rarely been considered [5]. However, the range of 3D printable materials, such as polymers, ceramics, metals, and carbon-based materials, has expanded significantly over the past decade [1], and these materials can now be used as active catalytic sites, catalyst substrates, and reactor reservoirs [5]. Micro fuel cells are also produced by laser-based additive manufacturing because of their long-lasting, thermally and chemically inert characteristics [6]. In this study, 3D fuel cell patterns were designed and additively manufactured using the most precise commercial 3D printers and photo-curable resin material. This newly developed method allowed the flow field plates to be tested. In addition, different printing parameters and the method to control surface roughness and create internal voids were tested to determine the effects on the mechanical and flow properties of the fuel cell channels. One advantage of 3D printing fuel cells is ultrafast prototyping with high quality [7]. Among the various types of micro fuel cell 3D printing methods, direct inkjet printing (IJP), selective laser sintering (SLS), robocasting, Digital Light Processing (DLP), and stereolithography (SLA) are preferred due to higher density achievement [8], [9]. This research uses digital light processing with the aim of introducing a dimension of chemical engineering in terms of additive manufacturing technology. This study tries to introduce innovative design principles that improve the efficiency of catalysis processes and fuel cell structure. The application of digital fabrication technologies in continuous flow reactions is one of the most critical opportunities for process intensification due to the use of heterogeneous catalysts or limitation by mass,

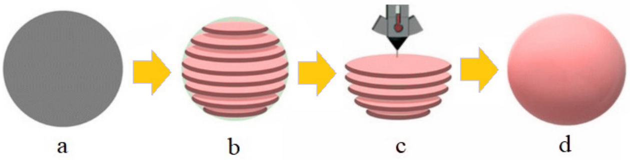

Fig.1. 3D printing process: (a) 3D structure designed with CAD software and then converted to StL 3D printable file format, (b) the digitally sliced model, (c) the layer-by-layer printing part, and (d) the final part.

momentum, or transfer in the reactor [5].

Different extrusion methods, such as material ink printing, resin photocuring, and powder-based methods, are the additive manufacturing tools that will significantly impact chemical engineering in fuel cell and catalytic technologies.

In additive manufacturing of solid oxide fuel cells, the porous microstructure electrode requirements should be considered in choosing the proper 3D printing method [10]. A mobile extrusion head can be used to make a part using selective layer-wise deposition of materials. The capabilities of this method to rapidly fabricate metals, polymers, composites, and ceramics using extrusion pastes containing those particles has proven in other researchs. The appropriate paste properties of the particle suspension make it possible to maintain the shape of the deposited layers while drying. In some printing processes, the printed part is subjected to secondary processing to remove viscosity and add mechanical stability modifiers. The minimum printable dimension in extrusion processes is generally between 100 and 500 micrometers [1], [8]; the fused deposition modeling (FDM) method works in much the same way.

In 3D inkjet printing, tiny droplets of liquid ink are sprayed onto a substrate at specific locations. In this printing process, print pulses are generated based on the digital data sent. Each pressure pulse results in a drop from the printer head. Pressure pulse stimulation is usually done through a thermal or piezoelectric actuator. Commercial inkjet printers typically drop 30-125 μm droplets at high speed with an optimal resolution of close to 100 μm [1]. However, the type of printable ink depends on the nozzle's geometry, size, and the type of stimulation. Newtonian fluids are one of the most common printable inks with a viscosity of less than 40 cP; surface tensions more than 20 dynes*cm^{-1} are adjusted by adding polymers and surfactants [4]. In the 3D printing process, these extra components, either as solutions or pre-formed particles, must be removed during post-processing operations.

The concept of multiscale modeling has been explored to couple the reactions of solid surface catalysts with computational fluid dynamics (CFD) to describe the complexity of heterogeneous catalysts in continuous flow reactors. A practical example is the study of flow hydrodynamics at different flow rates in various Advanced Flow Reactors (AFR) and Lead-Cooled Fast (LFR) reactors [4]. It is noteworthy that 3D printing allows the construction of reactors with computer geometry optimization. The shape of conventional reactors, for example, a cylindrical shape, is determined mainly by the cost of their structure or the limitations of conventional construction methods. Recently, the use of small flow reactors with channel cross sections ranging from a few micrometers to millimeters has dramatically increased [5]. A high degree of control over the reaction parameters in flow reactors is essential to achieve rapid mixing and efficient heat and mass transfer. Fully or partially 3D-printed reactors will play an important role in industry due to better control and scalability. While other flow reactors will likely be developed for 3D printing, batch reactors were the first examples of custom-made reaction vessels. Parra-Cabrera et al. showed how the clever selection of polymer materials leads to the use of custom 3D-printed reactors.

2. Experimental

Although commercial alternatives exist, they can be prohibitively expensive, and because they are required to optimize synthesis protocols, they lack the rapid design iterations possible with digital fabrication. An example of a custom reactor used to facilitate an artificial flow in the laboratory is a 3D-printed polypropylene FDM reactor. It should be noted that SLA and DLP have the best precision (<50 μm) and enable tight flow paths and complex internal structures. These photopolymers typically have a high glass transition temperature (>100 °C) and decompose in strong solvents [5]. Manufacturing using 3D printers also enables the construction of geometric reaction tanks and complex microreactors with integrated catalysts. It is used to make master molds, taking into account the expected shrinkage during coagulation [11].

This work used theoretical studies on the optimized geometries of catalytic substrates and fuel cell flow field plates to design 3D printed patterns in Solid Works software CAD. This literature review was done considering the most innovative design principles that are not applicable in other manufacturing methods. Then, the slicing process was performed using DLP-specific slicer software to achieve the best process and part properties. The next step was layer-by-layer fabrication using the Ayhan iResin 3D printer. In this process, acrylate, benzyl dimethyl ketal, acyl phosphine oxides, and α-aminoketones were used as photo-curable resins that were cured with a 99% ethyl alcohol solution and post UV curing. Post-curing was performed in a high-power UV curing chamber for 10 minutes at 50 degrees Celsius. The wavelength of the curing unit was 390 nanometers. Since the complex design is productive, the substrates and flow field plates were successfully fabricated using the 3D printer. In addition, various printing parameters, such as the part's orientation during printing, the thickness of the layers, and the method of creating internal voids, were tested to determine their effects on surface finish, mechanical properties, and flowability.

In fuel cells, polymer electrolyte membrane (PEM) components with no distortion are essential to avoid leakage of the reactant gases. Figure 2 represents the design of micro fuel cells in group *a* with different flow field apertures that could be produced via 3D printing methods. The design of a flow field plate (FFP) has been demonstrated to be an efficient way to improve electrochemical performance.

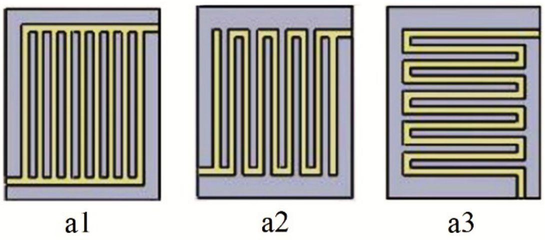

Fig. 2. Schematic of designed FFPs in the group a topological arrangement.

The FFP design is essential to deliver hydrogen to the anode and oxygen to the cathode. Figure 3 shows the different flow patterns for fuel cells in group *b*.

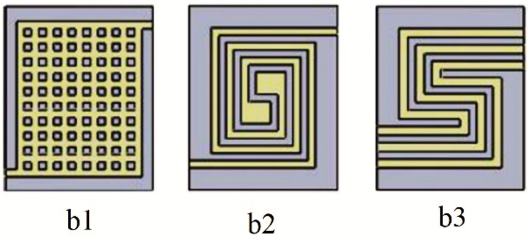

Fig.3. The schematic of designed FFPs in group b topological arrangement.

Undoubtedly, rapid, additively manufactured models of the designed FFP would be helpful for visual inspection and experimental flow testing. Biomedical stainless steel can also be 3D printed to achieve good chemical and mechanical properties, but there are some cost and accuracy concerns with metal 3D printing. However, in this research since it is limited to 3D print with high accuracy and cost efficiency [12], [13], photo-curable polymers are used instead of metals. Recently, 3D printing of ceramic suspensions using fused deposition modeling (FDM) technology has been discussed. However, most results show that the accuracy of this technology is not satisfactory for printing micro fuel cells (MFCs) [14].

In this study, experimental tests were also conducted using spatial diamond and octahedral lattice. Figure 4 shows 3D-printed parts with a directed geometry that cannot be fabricated by any other means than 3D printing. This substrate was developed to obtain a functionally directional catalyst for specific and smart applications. While it was not coated for testing in real conditions in this study, the functionally graded surface modification is important for the performance factor of catalysts.

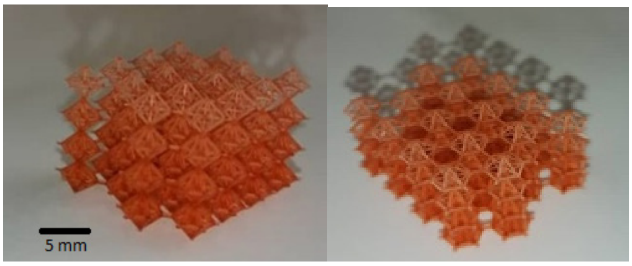

Fig. 4. Two 3D-printed diamond and octahedron scaffolds with a directional mesh foam configuration for use as a structural catalyst (left: rod size 800-100 µm, right: rod size 500-200 µm).

The photo-curable resins used in this research to fabricate plates are acrylate, benzyldimethyl ketals, acyl phosphine oxides, and α-aminoketones. In addition to photo-curable polymers, DLP printers will soon be able to print ceramic slurries. The advantages of the DLP method are high printing resolution, fine features, microporosity, cost efficiency of polymers, low material waste, and high-density structure [15], [16]. The samples shown in Figure 6 were printed using an Ayhan-iResin 3D printer, and the fluid passage between the grooves was tested. The patterns printed using resin technology were ready after curing with 99% ethyl alcohol solution and 405 nm UV curing for 150 s. Figure 7 shows the test samples masked by a black layer for better measurements, and the names are listed in Table 1.

Table 1. Designed and Additively Manufactured Fuel Cell Sample Patterns and Geometrical Specs

Sample code	Groove Geometry	Channel size	Surface Area
a1	Parallel	mm 0.6	cm2 1.9
a2	Interdigitated	mm 0.6	cm2 2
a3	Serpentine	mm 0.7	cm2 2
b1	Pine	mm 0.8	cm2 2.1
b2	Spiral	mm 0.6	cm2 2
b3	Meander	mm 0.6	cm2 2

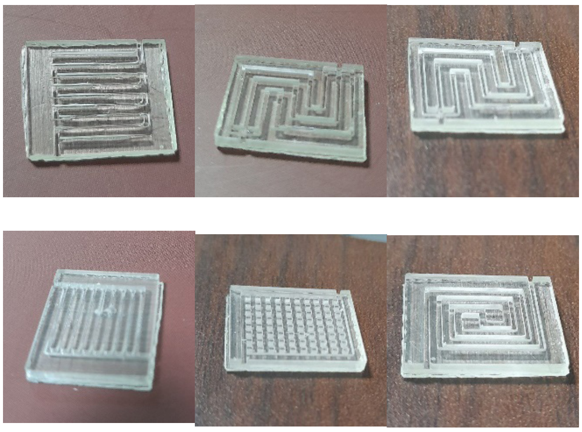

Fig. 5. 3D-printed test samples using a precise DLP machine right after printing.

3. Results and discussion

Computer-designed 3D patterns were printed using a photo-resin 3D printer with a photo-curable resin. Various changes in printing parameters, such as the part orientation during printing, the thickness of the layer, and the method used to create internal voids, were tested to determine the effects on printability and subsequent mechanical properties. In addition, the results of surface measurements and fluid flow tests indicated that this printing method appears capable of producing fuel cell flow field plates. Further flow tests with distilled artificial water and ethyl alcohol were also conducted in the laboratory. The results confirm that the importance of digital manufacturing is increasing in this field. Also, the increasing prevalence of 3D printers is accelerating access to these devices and enabling creative collaboration between chemical and mechanical engineering researchers. This study approach focuses primarily on improving mass transfer through geometry optimization. However, printed catalysts and reactors with chemical functionalities point to considering more prosperous opportunities in the design [17]. Given the rapid evolution of 3D printers' performance, such as high-performance heads, the integration of digital control over geometry, performance, and chemical composition in catalysts and structured reactors is proving to be of interest to researchers [18] [19].

However, much progress is still needed in areas such as reducing printing costs, controlling internal reactor surface roughness, and standardizing test protocols, to name a few. New approaches will help solve these challenges. For example, the orientation of the part during printing, the thickness of the layer, and the method used to create internal voids all affect the roughness of the internal surface of reactors. Figure 6 shows other examples of printed catalytic reaction devices.

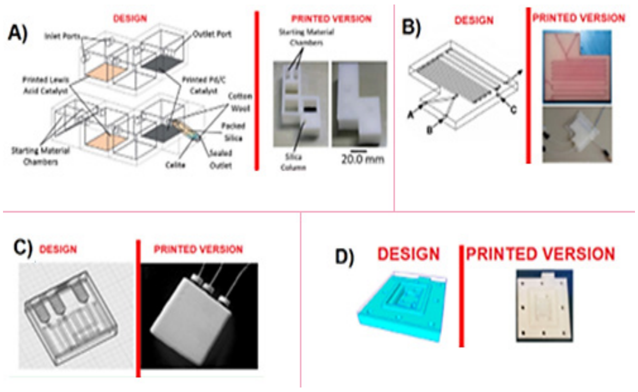

Fig. 6. (a) Design and final version of a 3D-printed sequential reactor, (b) Final design and version of a 3D-printed miniature fluid reaction device, (c) Final design and version of a 3D-printed conical distributor and a reactor that are both integrated used for biodiesel synthesis. (d) Design and final version of a 3D-printed electrolyzer cell component for water splitting [5].

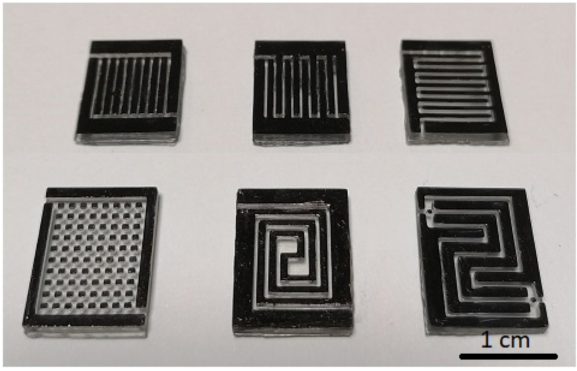

Fig. 7. 3D-printed samples with upper indicator film for better-measuring contrast using an Ayhan-iResin 3D printer.

The results of the tests performed on the printed samples and the analysis of the possibilities that can be exploited with 3D-printed fuel cells are shown in Table 2. This table compares the potential of this manufacturing approach with traditional methods, as presented in studies done in this area. While only an assessment of the possibilities and difficulties was made due to the complexity of the tests and the application in real fuel cell test settings, the results are essential for clarifying the design and production of innovative fuel cells. It can be concluded that the 3D and complex geometry that can be produced by 3D printing will enable the use of higher efficiencies in fuel cells.

Table 2. Characteristics and limitations of 3D printed fuel cells compared to conventional methods.

	Property	Description	Challenges
1	Mechanical properties	Developable and good bending properties	3D printing of some composite materials
2	Electrical properties	Designable and good electrical conductivity	3D printing of some conventional materials
3	Gas diffusion	Possibility of control porosity and permeability properties	3D printing of some conventional materials
4	Liquid flow	Fully controlled flow	Almost no challenges
5	Density	Possibility of changing porosity and tailored density	3D printing of some conventional materials
6	Poisson's ratio	Possibility of using mechanical metamaterials	Limitations of some materials

For the commercial production of small- to medium-sized batches of catalysts with customized geometries and sizes, the 3D-printed catalyst is a unique and applicable research tool. Printed ceramic mesh filters are already used in adjustable filtration for molten metal casting. The next option is structured internal columns for reactive distillation and 3D printing chromatography. 3D-printed metal grids give interesting features to heat exchangers. Preliminary investigations show that the heat transfer rate in a stainless steel gyroid plate heat exchanger is much higher than in other models, such as a flat plate, shell, or tube-like shapes[13]. By changing the porosity of the substrate, a transformation is formed near the inlets or outlets. Additive manufacturing has recently gained attention for use in flow reactors at the laboratory scale and for industrial production. In the pharmaceutical and chemical industries, for example, the use of batch reactors in production depends on the protocols used in the synthesis of laboratory-scale products. It is well established that introducing flow chemistry at the laboratory scale enables the discovery and scale-up of synthesis conditions and makes possible products that are currently unattainable in industrial production [5]. The role of additive manufacturing in continuous flow production also increases with the increase in thermal and chemical compatibility of AM materials.

Conclusion

This study tested common 3D printing methods in flow chemistry, and the results showed that the comparisons differed in terms of chemical and thermal stability, engineering and design constraints, and achievable accuracy. A comparison between conventional fuel cells and the printed segment showed that using 3D printing to produce fuel cells efficiently creates a larger contact area between the flow field plate and the gas diffusion layer in closed channel flow field plates. It is well known that water management is an essential parameter in fuel cell plates. This research showed that 3D-printed plate parts have a better aspect ratio and performance to keep the membrane hydrated, avoid water accumulation, and ensure gas distribution on the electrode surface. In addition, the efficiency of the directional catalytic substrate grids is higher, resulting in more controlled and efficient catalytic sites. 3D-printed reactors primarily meet the changing needs of research laboratories and can be designed and manufactured to perform a variety of experiments, up to and including environmental analysis. Additive manufacturing helpfully enables the fabrication of fuel cells, leading to the prototyping of different variants of flow field topologies and channel profiles. Finally, AM offers cost efficiency, high aspect ratio designs, and impact design. The horizon ahead of additive manufacturing technology for catalysts and fuel cells is also much broader, and many production advantages remain to be achieved.

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