FABRICATION OF CERAMIC FILAMENT FOR 3D PRINTING CERAMIC DEVICES

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Abstract

The purpose of this research was to investigate the concept of 3D printing ceramics by using a thermoplastic-ceramic composite filament. Because of the struggles currently being faced with the manufacturing of ceramics, this technique could provide an inexpensive solution to the fabrication of advanced ceramic technologies, namely the solid oxide fuel cell (SOFC). The SOFC was focused on because when used in the reverse mode, it can provide a solution to producing oxygen from the Martian atmosphere. The objectives included creating the composite filament, printing small samples, sintering the samples, and observing the samples' surface after sintering using a scanning electron microscope (SEM). It was found that while the samples became porous after sintering, they also became flaky and delicate. Future research includes exploring other techniques for sintering to improve the end product and exploring other thermoplastics.

Introduction

Ceramic production, while often a costly and time-consuming process, is an important factor to consider when investigating advanced ceramic technologies. Because of its disadvantages, ceramic production presents a major problem for utilizing such technologies. For this project, the ceramic solid oxide fuel cell's (SOFC) manufacturing process was focused on due to its high efficiency as a fuel cell and its connection to energy production and a manned mission to Mars.

The SOFC is a high temperature fuel cell that consists of a ceramic electrolyte and two ceramic electrodes. It takes in fuel (usually hydrogen) and oxygen (usually from air) to produce electricity and water. The reactions that occur to yield this result happen in the anode and cathode layers. Air is taken in at the cathode while fuel is taken in at the anode. At the cathode, oxygen ions are produced from the air which then travel through the electrolyte to the anode. At the anode, hydrogen (the fuel) is oxidized by the oxygen ions to produce water and electricity[1]. Figure 1 shows this process of producing electricity with the SOFC.

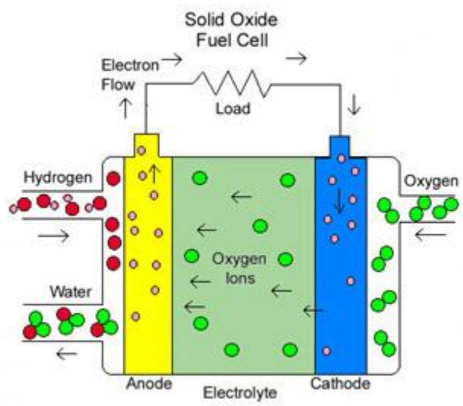

Figure 1. Electrochemical process of the solid oxide fuel cell (SOFC)[1].

By improving the cost of manufacturing the SOFC, it could become a major device used for energy production as alternatives to fossil fuels are searched for. Additionally, it could provide a solution to one major obstacle of a manned mission to Mars—the lack of oxygen in the planet's atmosphere. The Martian atmosphere consists of 95% carbon dioxide and merely 0.13% of oxygen[2]. It is not feasible to transport the needed oxygen to Mars because of the added weight and cost. Therefore, the alternative is to produce oxygen while on Mars. This can be done by using the SOFC in the reverse mode, otherwise known as the solid oxide electrolysis cell (SOEC). Besides splitting water, SOFCs can also be used to electrolyze CO_2 to produce CO and O_2. The SOFC would take in the abundant CO_2 in the atmosphere to yield oxygen for Mars missions[3]. This idea is what the Mars Oxygen In-Situ Resource Utilization Experiment (MOXIE) aims to prove with the unmanned mission in 2020—that oxygen can be produced on Mars[4]. However, to make this a practical solution, the manufacturing of SOFCs needs to improve in several areas such as cost, precision, and automation[5].

The current processing methods of ceramics to produce SOFCs include tape casting, screen printing, pressing, extrusion, and calendering. While pressing and extrusion can result in planar or tubular geometries, tape casting and calendering only produce planar geometries[6]. This limits what designs tape casting and calendering can be used for. The disadvantage of pressing is the extra time spent and the disadvantage of extrusion is the material consumed[6]. The concept of producing a filament for 3D printing can provide a low-cost and fast fabrication solution to ceramic manufacturing that has high versatility.

Filament Production

The thermoplastic- ceramic composite filament was created from a combination of Nylon 12 and Lanthanum Strontium Manganite (LSM) powders. The particle sizes of the powders for Nylon 12 and LSM were 45 µm and 0.48 µm respectively. These small particle sizes of the powders helped to create a close to homogenous mixture.

The mixture was composed of 45% LSM- 55% Nylon 12 by mass and was mixed using a ball mill (Jar Mill, US Stoneware, Palestine, OH) for 24 hours. A filament extruder (Filastruder, Snellville, GA), seen in Figure 2, made the powder into a filament by melting the powder and extruding it through a nozzle using a rotating feed screw. Because the extruder depends on a feed screw, the thermoplastic must be melted throughout the barrel. Initially, the extruder was set to about 220°C, allowing the powder to thoroughly melt in the chamber. Once melted, the temperature was reduced to 190°C so that when extruding, the filament had a large enough diameter for 3D printing. If it was kept at 220 °C, the filament would rapidly extrude, resulting in too small diameters. Conversely, too low of a temperature would cause the thermoplastic to become too viscous and it would not extrude.

Figure 2. Filament extruder.

3D Printing Ceramic Filament and Sintering

The Maker Select Plus (Monoprice, Rancho Cucamonga, CA) 3D printer was used for printing the composite filament. Because of the high extrusion temperatures required for 3D printing, an all metal hot end was installed in the printer's extruder assembly. 240°C nozzle temperature and 80°C bed temperature were used. Also, a 1 mm nozzle, instead of the common standard 0.4 mm nozzle, was used because the composite filament easily clogged the smaller nozzle diameter. Circles with 30 mm and 16 mm diameters and 3 mm in thickness were printed.

Once the circles were printed, they were sintered with various procedures with a furnace (KSL-1700X, MTI Corporation, Richmond, CA) with a maximum temperature of 1700°C. All procedures included a two hour hold at 250°C, a temperature increase rate of 1 °C/min, and a temperature decrease rate of 2°C/min. The hold period at 250°C was done so that the Nylon would have time to boil slowly. If boiled too quickly by immediately going to the peak temperature, the sample would bubble rapidly, possibly destroying it.

The four sintering procedures used are documented in Table 1. Following sintering, a scanning electron microscope (SEM) (Phenom ProX, Micromeritics, Norcross, GA) was used to view the surface of the samples.

	Peak Temperature (°C)	Dwell time (hr.)
1	900	4
2	1000	8
3	1000	16
4	1000	24

Table 1. Sintering procedures.

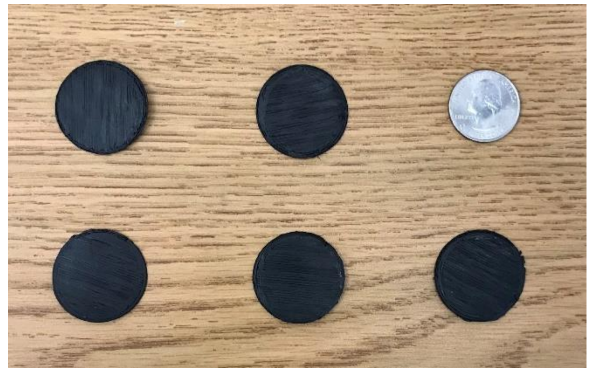

Figure 4. Nylon-LSM printed samples.

Results and Discussion

The filament created was consistent and had great flexibility, as seen in Figure 3. For filament to be feasible in the future, flexibility is important for the ease of 3D printing and storage. While the filament initially had rough edges, light sanding was able to even out the diameter and ensure a smooth passage through the 3D printer nozzle assembly.

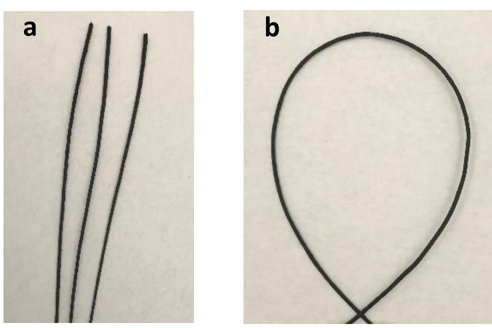

Figure 3. a. Nylon-LSM filament; b. flexibility of filament.

The 3D prints for the simple circle were uniform, accurate, and repeatable. Layers adhered well together and there were no gaps in the print caused by the filament not extruding well. The samples were not fragile, making handling easy. Some printed 30 mm diameter circles can be seen in Figure 4.

After all sintering procedures, the ceramic samples became flaky and very delicate. Instead of remaining intact like the 3D printed pieces, the sample broke apart after sintering. Care had to be taken while handling so that the pieces would not break and turn into powder. Increasing dwell time increased the sizes of the pieces and typically, the larger pieces were found with the 16 mm diameter circles rather than the 30 mm diameter circles. Samples before and after sintering can be seen in Figure 5.

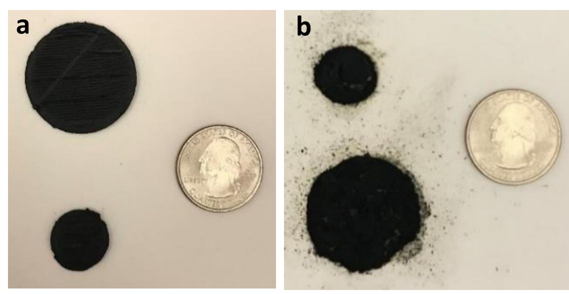

Figure 5. a. Before sintering; b. after sintering.

The porosity and surface of the samples of the different sintering procedures were viewed with the SEM. The flakiness of the samples' surface can be seen, especially in Figure 6a and 6c. The porosity of the sintered samples, important for gas diffusion in the SOFC, can be seen in Figure 6a-d with a green state (not sintered) sample for comparison in Figure 6e.

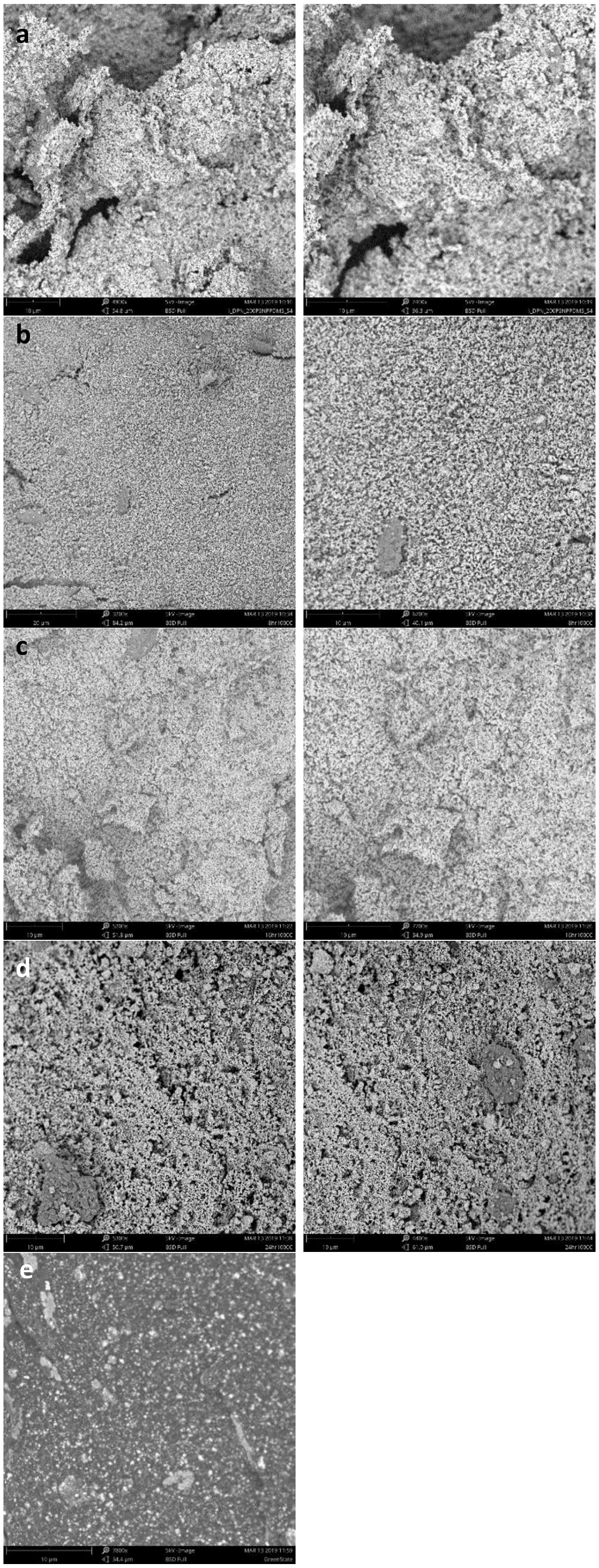

Figure 6. Sintering procedure from Table 1: a. 1, b. 2, c. 3, d. 4; e. green state sample.

While the filament created was able to be 3D printed and sintered, there are areas that could be improved. The filament has an inconsistent diameter due to gravity as the filament is extruding. While it was not an issue during this experiment, it could lead to problems in the future for 3D printing more complex or larger objects. Other areas for future research include exploring different sintering procedures and different thermoplastics to use for the composite filament.

Conclusion

Nylon 12 has proven to be a viable candidate as a thermoplastic for 3D printing ceramics. The composite filament created was flexible and consistently able to be 3D printed. As expected, the sample is porous after sintering due to the thermoplastic boiling off. Different thermoplastics and sintering procedures can be investigated to improve results. With more research and experimentation, this method can decrease the time and cost required for fabricating ceramic devices, making their applications more practical in the future.

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