Minary Lab, UTDallas

Report 03/20/2023

Accomplishments

- Created a process flow for 3D printing 8YSZ ceramic parts
  - Photocurable slurry preparation, DLP printing and sintering, thermal analysis
- Identified requirements for printable and functional 8YSZ anode CAD model
  - Porous 8 mol% yttria-stabilized zirconia as anode-supported SOFC
- Established a parametric surface equation for the 8YSZ electrolyte contact surface
  - Custom parameter for relative surface area increase
  - Flexible surface geometry
  - Numerical calculation of surface area
- Designed a preliminary 8YSZ anode CAD model in Creo Parametric
  - Adaptable design
  - Fully flexible dimensions
  - Simple to fine-tune and regenerate in model space
- Revised project requirements and implemented changes to 8YSZ anode CAD model
- Analyzed surface area of CAD model in-workspace for various parameters
  - Produced a rough estimates of relative surface area increased based on geometry

Planned Work

The primary objective of this project is to determine a method for printing 8YSZ using DLP, with the eventual goal of manufacturing an improved design for the anode supported flat tube SOFC. **Table 1** identifies some critical parameters for a successful project. Additionally, four personal objectives to accomplish this goal are identified below. This is an iterative process, where previous steps may need to be revisited once knowledge is gained.

(1) Familiarize myself with lab equipment, materials, and available resources

- Understand how to operate equipment, and the capabilities / limitations of equipment specific to the lab
  <u>Primarily includes</u>: DLP printer, ball mill, tube furnace, and sintering furnace
  - Discussions and demonstrations from Moein, Dr. Minary, and other lab members
  - Read user manuals and informational documents
  - Personal research
- Discern the specific properties of materials available in the lab
  <u>Primarily includes</u>: 8YSZ, photocurable resin, and any necessary additives such as solvents, dispersants, or pore formers
- Learn safety and general lab procedures to feel comfortable working independently
- Consider computational analysis tools, such as COMSOL fuel cell module

(2) Prepare a printable 8YSZ resin slurry

- Formulate a detailed recipe
    - Coordinated with Moein
    - Preform research and determine any knowledge gaps
    - Predict challenges or uncertainties in the process
- Get recipe approved by Dr. Minary
- Prepare in lab, record all procedures and results
    - Consider if any testing for slurry properties is necessary

(3) Print and post-process 8YSZ resin slurry

- Determine all necessary print, debinding, and sintering details
    - Coordinate with Moein
    - Personal research
- Prepare final CAD model
    - Consider printing multiple designs of 8YSZ anode on single build plate
    - Convert STL using slicer
- Print slurry in DLP printer
    - Consider quality of green body print
    - Record all procedures and results
- Clean, debind, and sinter green body
    - Consider quality of sintered part, especially observing any cracking
    - Record all procedures and results

(4) Analyze and test final product

- Determine relevant material properties and standard testing procedures
    - Focus on SOFC applications
- Classifications may include microstructure (porosity, pore size, grain size distribution), thermal and mechanical durability (mass loss in heating, energy absorbed when heating or cooling, strength, fracture toughness), electrochemical properties (ionic conductivity, activation energy)

Table 1. Important properties to consider during each step of the process

Model Parameters	Corrugated Surface	Corrugation amplitude
		Corrugation period
		Crosswave amplitude
		Crosswave period
	Channels	Diameter
		Cross-section shape
		Number
		Position
		Path (i.e. sine curve)
	Other geometry	Overall size
		Interconnect height
		Rounded edge curvature
Slurry Parameters	Materials	Photocurable resin (photoinitiator, monomers, oligomers)
		Solvent
		Dispersant
		Pore former
	Composition	Weight or volume fraction
		Solid loading
		Particle size distribution
		Mean particle size
		Single or multiple ceramic powder sizes
	Printability	Viscosity
		Light scattering
		Refractive index contrast
Print Parameters	Dimensions	Layer thickness
		Hatch spacing
	Laser	Power
		Velocity
		Wavelength
	Resultant properties	Cure depth
		Cure width
Post-Processing Parameters	Debinding	Temperature
		Temperature ramp
		Time held
		Airflow
	Sintering	Temperature
		Temperature ramp
		Time held

Additional Project Details

Requirements for 8YSZ Anode CAD Model

Create a 3D CAD model of a DLP printable 8YSZ anode, improving electrolyte and fuel channel contact area relative to the anode supported "flat-tubular SOFC" design.

- The CAD model must have an electrolyte contact surface, interconnect contact surface, and lengthwise internal fuel channels.
  - Dimensions of the CAD model should be approximately 15mm x 50mm x 3mm (width x length x height).
- The active surface area for both the electrolyte contact surface and fuel channels must be increased relative to a flat surface.
  - The electrolyte contact surface should use oscillatory corrugations to increase relative surface area.
  - Fuel channels should use non-cylindrical paths to increase relative surface area.
- The geometry and dimensions of the model must be manufacturable using ceramic AM; the design must be printable using an 8YSZ slurry in a DLP printer, and must survive post-processing and sintering without cracks.
  - The cross-sectional wall thickness should be approximately 1mm throughout.
  - The CAD model should round edges, avoiding sharp edges and corners.
- The CAD model should be stable in design, allowing for dimensions and features to be edited without issue.
  - Major dimensions should be input as Creo parameters.
  - All other model features should be related to parameters using Creo relations or workspace constraints.
- The relative surface area increase should be simple to determine.
  - The electrolyte and fuel channel surfaces should use sine curves as basis for increased surface area.
  - The whole electrolyte and fuel channel surfaces should be expressible by an equation.

Equation for Electrolyte Contact Surface

Relative increase in electrolyte surface area contact is achieved using two sine curves. A flat x-y plane can be transformed using a sine curve in the x-z plane, where z is a function of x. This creates peaks and troughs of the surface, and therefore referred to as the "**corrugation**" curve. Surface area of the corrugated surface may further be increased using a sine curve in the x-y plane, where x is a function of y. This creates the wave along the length of the peaks and troughs, and therefore is referred to as the "**crosswave**" curve.

This creates a pattern of wavy corrugations, as depicted in **Fig. 1**, which is modelled with a general parametric surface in equation (1). This equation relates height position (z-axis) as a function of width position (x-axis) and length position (y-axis). A_x and A_y express the amplitude of the corrugation and crosswave sine curves, respectively, while T_x and T_y express the periodicity of the corrugation and crosswave sine curves, respectively.

The surface equation is especially useful as a tool for numerical calculation of relative surface area. The double integral in equation (2) gives the general formula for surface area in any flat rectangular region on the x-y plane. Finding relative surface area increase is then simplified in equation (3) by recognizing the repeating nature of the wavy corrugation pattern, where surface area in the region bounded by $x = [0, T_x/2\pi]$ and $y = [0, T_y/2\pi\,]$ represents one full period of the corrugation and crosswave curve. Assuming the full surface has a length and width that is modular of their respective sine curve periods, the relative surface area increase of the whole region is the same as the relative surface area increase for any other modular region.

$$f(x,y) = A_x \cdot sin\big(T_x \cdot x + A_y \cdot sin(T_y \cdot y)\big) \tag{1}$$

$$SA = \int_c^d \int_a^b \sqrt{|f_x(x,y)|^2 + \left|f_y(x,y)\right|^2 + 1}\, dx\, dy \tag{2}$$

$$SA_{rel} = \frac{\int_0^{\frac{T_y}{2\pi}} \int_0^{\frac{T_x}{2\pi}} \sqrt{A_x^2 \cdot \cos^2\big(T_x \cdot x + A_y \cdot \sin(T_y \cdot y)\big) \cdot \big({T_x}^2 + A_y^2 \cdot {T_y}^2 \cdot \cos^2(T_y \cdot y)\big) + 1}\, dx\, dy}{\left(\frac{T_y}{2\pi} * \frac{T_x}{2\pi}\right)} \tag{3}$$

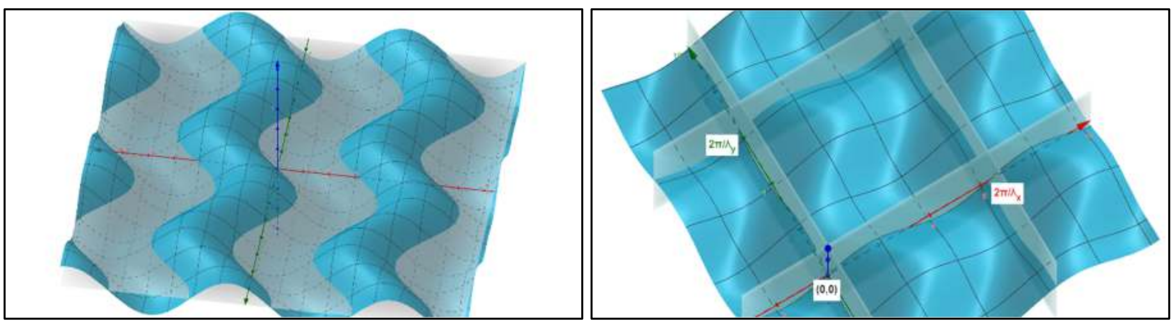

Fig. 1. Parametric surface of equation (1) (left) and bounded region of corrugation period by crosswave period (right)

Design Parameters and Dimensions of 8YSZ CAD Model

The CAD model incorporates the above surface by sweeping the corrugation curve along the crosswave curve, maintaining constant normal direction. The channels are also swept along the same crosswave curve, and are centered at each peak of the electrolyte contact surface. All dimensions of the model were defined with customization in mind; **Fig. 2** illustrates a change in model parameters. **Fig. 3** shows the latest iteration of this model after updating and improving problem definition.

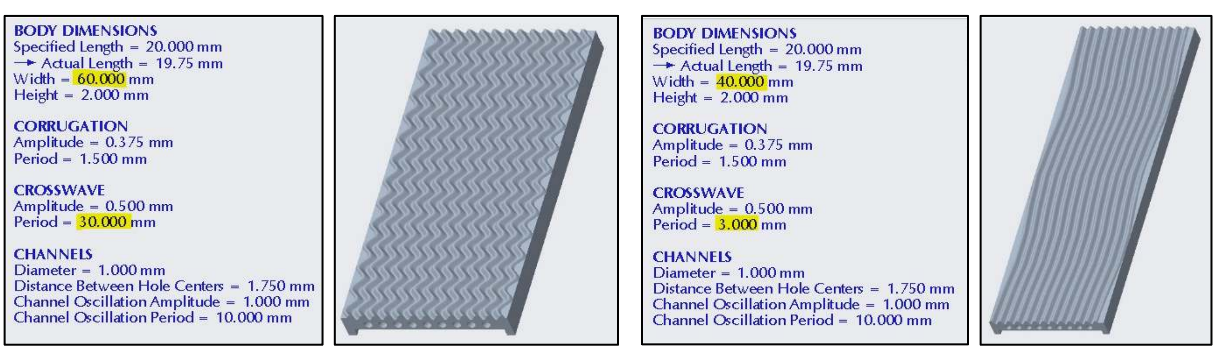

Fig. 2. Changing the width and crosswave period parameters in model workspace

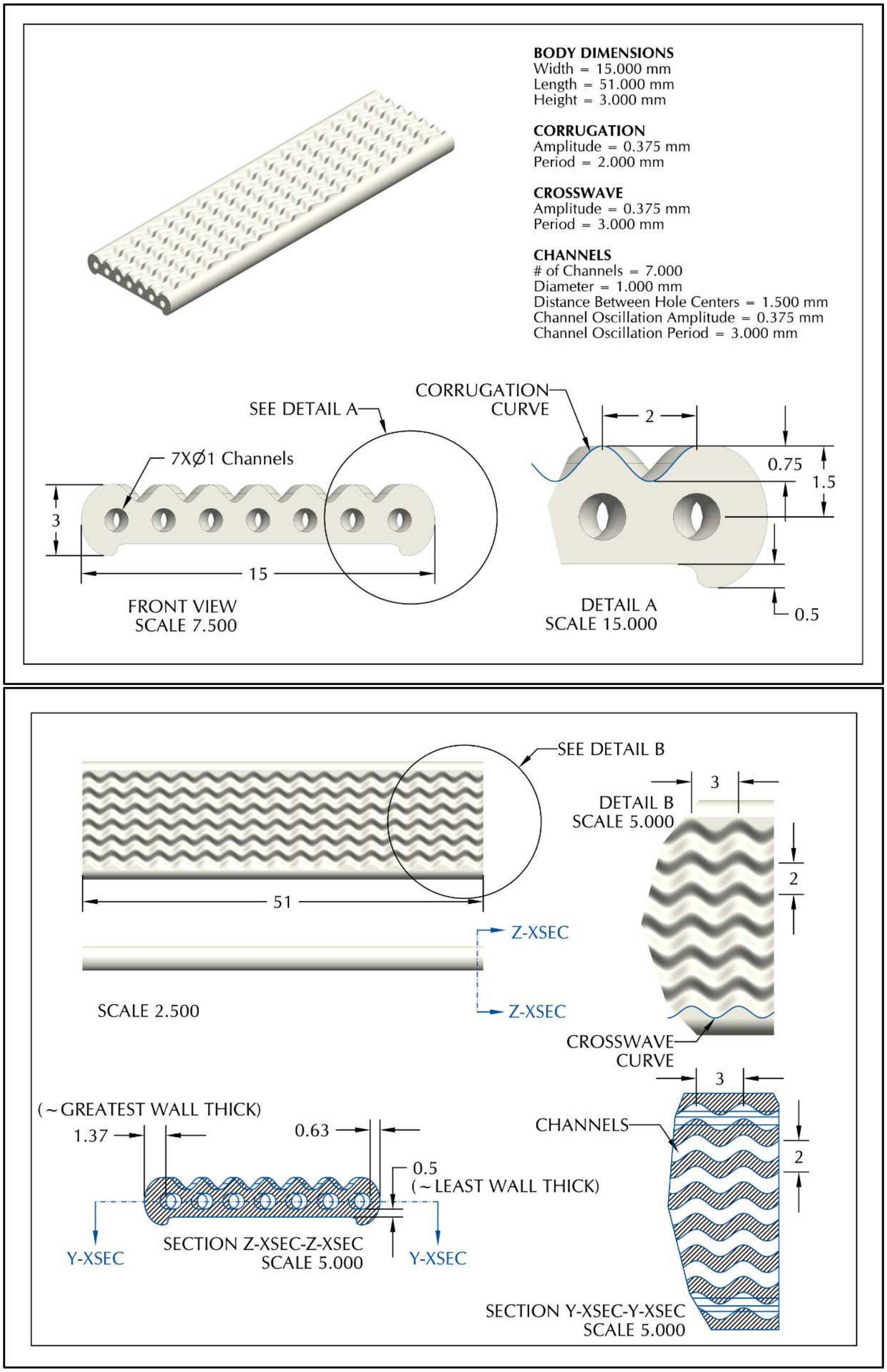

Fig. 3. CAD drawing with improved design of 8YSZ anode

Approximated Surface Area as a Function of Design Parameters

Table 2 lists various possible configurations of surface parameters (amplitude and period of corrugation and crosswave curves) alongside the resultant relative surface area (SA) increase. Surface area was measured directly in the Creo Parametric model space after editing and regenerating the model, then divided by the SA of a similar size flat surface (same width x length) to produce approximate results of relative SA increase. The first row of results uses dimensions shown in **Fig. 3**, subsequent rows contain highlighted values to indicate a change from the first-row reference.

Table 2. Example parameter configurations and their relative SA increase

Corrugation Amplitude (mm)	Corrugation Period (mm)	Crosswave Amplitude (mm)	Crosswave Period (mm)	Relative SA Increase
0.375	2	0.375	3	**1.359**
0.375	**1.5**	0.375	3	**1.571**
0.75	**1.5**	0.375	3	**2.559**
0.375	**1**	0.375	3	**2.047**
0.5	**1.5**	0.375	**2**	**2.055**
0.375	2	**0.5**	**2**	**1.544**