Printed Fuel Cell Electrodes with Engineered Porosity

Prasanna Khatri-Chhetri[1], Denis Cormier[1], Fanglin (Frank) Chen[2], Prasun Majumdar[2]; [1] Rochester Institute of Technology, Department of Industrial and Systems Engineering, Rochester, NY 14623; [2] University of South Carolina, Department of Mechanical Engineering, Columbia, SC 20208

Abstract

Solid Oxide Fuel Cells (SOFC's) are complex electrochemical devices whose designs require consideration of mass transport, electronic and ionic conductivity, and thermal management. Traditional SOFC fabrication techniques produce electrodes whose random pore geometries are not necessarily ideal with respect to the cell's functional requirements. This paper details initial experimentation involving novel multi-material direct-write printing techniques whose aim is to produce anode and cathode layers in which pore size and shape have been tailored to improve cell performance. Optical and electron microscopy are used to characterize the direct-write printed porous electrodes.

Introduction

This paper focuses on the use of direct-write material printing techniques to fabricate porous Solid Oxide Fuel Cell (SOFC) electrode (anode and cathode) layers. SOFC's are electrochemical devices that convert chemical energy directly into electrical energy without combustion. An attractive feature of SOFC's is their potential to use a wide variety of fuels including hydrogen, methane, butane, natural gas, diesel, gasoline, etc. Readers interested in an approachable introduction to fuel cells are directed to O'Hayre et al. [1].

SOFC's are primarily made up of ceramic materials (e.g. oxides of zirconium or cerium) and consist of no moving parts. The cells operate at relatively high temperatures (~600-900°C) which can produce exhaust gases that are ideal for use in combined heat and power applications and combined-cycle electric power plants.

Figure 1 illustrates the basic structure of a single cell. Current is collected via the interconnect layers. Channels in the interconnects direct the flow of oxygen over the porous cathode surface and a fuel (e.g. hydrogen) over the porous anode surface. Oxygen ions generated in the cathode are transported through the dense electrolyte layer. Oxygen ions reaching the anode side oxidize the fuel and create H_2O and heat as the primary byproducts. In addition to allowing gases to flow to active sites, the anode and cathode provide structural integrity to the cell. Although different cell configurations exist, the thickness of the anode or cathode layers does not typically exceed 100 µm. The electrolyte thickness is ideally in the 10-40 µm range. The porous electrode properties such as electronic, ionic, and thermal conductivity, porosity, tortuosity, and surface area all significantly influence the cell performance.

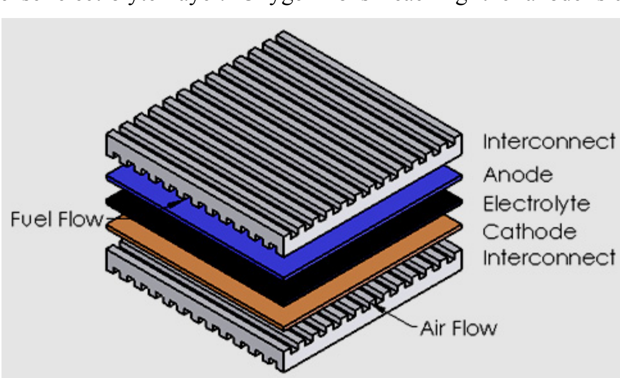

***Figure 1**. Exploded view of SOFC*

SOFC's are most often made using simple mass production techniques such as tape casting and silk screening. From a commercial point of view, these processes are very attractive due to their high speed and low cost. The anode and cathode layers, however, tend to have a homogenous pore structure and chemical composition. The aim of this paper is to explore ways in which Direct-Write material printing techniques can be used to introduce functionally graded material compositions and engineered pore morphologies in SOFC's.

Direct-Write Material Printing

Direct-Write (DW) printing technologies are a family of processes in which inks in the form of solutions and/or particulate suspensions are selectively deposited on a substrate to produce a functional object or to add to the functionality of an existing object. Hon et al. [2] provide an excellent overview of the different approaches to DW material deposition.

This paper focuses specifically on a form of DW material printing that involves microextrusion [3] that can optionally include multiple materials. Figure 1 shows an nScrypt microextruder tool with three ink reservoir inputs. After inks are prepared, they are loaded into 3cc plastic syringe barrels that feed

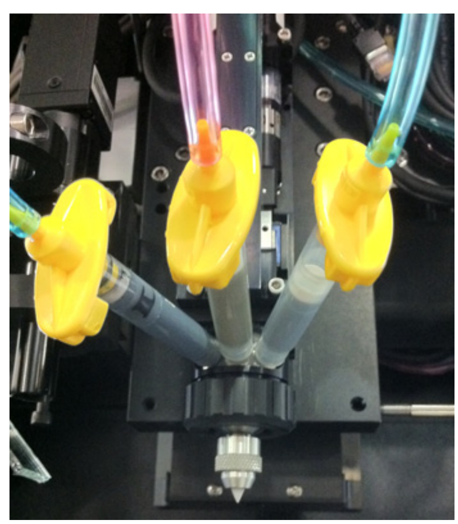

***Figure 2**. nScrypt 3 material micromix dispensing tool*

into the valve body through 10-32 threaded luer adaptors. Within the valve body, three independently controlled needle valves can be opened and closed under computer control during deposition to start or stop the flow of ink from a specific syringe barrel. Air pressure from 0-100 psi is independently applied to each syringe barrel to provide the force necessary to inject ink into the valve body mixing chamber. The magnitude of air pressure may be varied during deposition if desired so that the proportion of each ink component can be controlled. This allows one to print functionally graded materials. Where ink from each of the three syringe barrels meet inside the valve body, a mixing rod is used to uniformly blend the inks just ahead of the ceramic tip through which the materials are extruded onto the substrate. Ceramic tips with inner diameters ranging from 25-150 µm are typically used.

The microdispensing tool just described is mounted to a 3-axis stage with X/Y/Z travel of 300mm x 150mm x 100mm. The stated accuracy values are +/- 12 µm in X/Y and +/-6 µm in Z. The stated repeatability values are +/- 2 µm in X/Y and +/-1 µm in Z. The 6-axis Aerotech motion control system allows the microdispenser to move along the prescribed material deposition path while the needle valves and air pressures are simultaneously controlled as needed. Note that this system is capable of printing non-planar geometries with non-uniform material compositions. While it does not have the same throughput as other deposition techniques, it is extremely flexible in terms of what it can produce.

Graded SOFC Porosity Through DW Printing

From a scientific perspective, SOFC performance is highly complex and depends upon laws of physics that govern electrochemistry, thermodynamics, and fluid dynamics to name a few. Optimization of performance is extremely complex in the sense that gains in one area often result in losses in other areas. For instance, electrode layers with large open pores tend to have better gas permeability for the flow of oxygen and fuel. However, increased pore size is generally accompanied by a reduction in active surface area and triple phase boundary (TPB) length.

In recent years, a compromise between the need for good mass transport and high surface area has been made by grading the size of the pores from large to small. At the lab scale, this can be done by sequential uni-axial pressing of one layer of powder on top of the next where each layer of pressed powder has a different volume fraction of pore forming agent [4]. Pore forming powders such as graphite or starch burn off during sintering, hence the volume they previously occupied becomes a pore. Note that porosity through the thickness of the pressed disk can be varied with this method, but porosity within a given layer cannot easily be varied. Non-planar fuel cell geometries also cannot be produced via this method.

In the work presented here, the microextrusion DW material printing technique was investigated as an approach with the flexibility to grade porosity within a layer and to produce non-planar geometries. Ni-YSZ powder (Fuel Cell Materials) was used as the anode material, and Asbury TC307 graphite powder was used as the pore forming agent. Three ink formulations were prepared. In order to avoid inaccuracies associated with measuring powders by volume due to powder settling and/or compaction, powders were measured by mass. Formulations 1, 2, and 3 shown in Table 1 have 1 wt%, 3 wt% and 5 wt% pore former respectively,

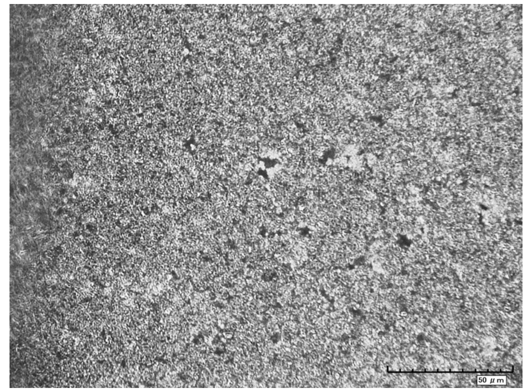

***Figure 3**. Ni-YSZ with 1 wt% graphite*

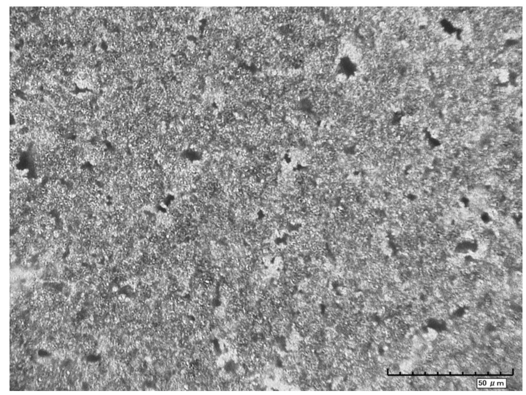

***Figure 4**. Ni-YSZ with 3wt% graphite*

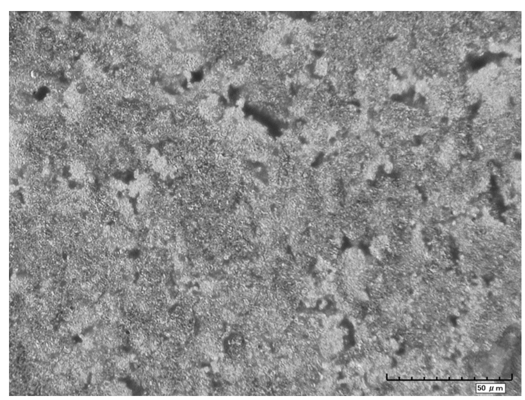

***Figure 5**. Ni-YSZ with 5 wt% graphite*

where the wt% is based on the total powder weight. Note that 1 wt% graphite pore former corresponds to approximately 10 vol%.

Table 1: Graded porosity in compositions

Ink Formulation	NiO-YSZ (g)	Graphite (g)	Ink Vehicle (cc)
1	4.95	0.05	5.00
2	4.85	0.15	5.00
3	4.75	0.25	5.00

All powders were weighed on a digital scale and then hand mixed with 5 cc of a terpineol-based ink vehicle (Fuel Cell Materials). The blended inks were then spun in a Thinky ARM 310 counter rotating mixer at 2,000 rpm for 20 minutes. Each ink was loaded in a 3cc syringe barrel and then printed into a uniform layer using an nScrypt SmartPump microdispensing tool. Printed samples were dried under an IR lamp and then sintered in air at 1,400˚C for 2 hours with a ramp speed of 5˚C/min. Figures 3, 4, and 5 show 1,500X optical micrographs of the three samples. The increasing degree of porosity in each sample is readily evident.

Following the Ni-YSZ feasibility trials, a samarium-doped ceria (Fuel Cell Materials) electrode layer with graded porosity was printed using a similar technique. Two 15 µm thick layers with 100% SDC ink (i.e. no pore former added) were first printed. The syringe was then changed, and two additional 15 µm thick layers with 85 wt% SDC and 15 wt% graphite ink were printed. The 60 µm thick electrode with graded porosity is shown in Figure 6. Although the feasibility of grading the porosity within the plane has not yet been demonstrated, it is conceptually straightforward to envision this being done using the 3-material micro-extruder shown in Figure 2.

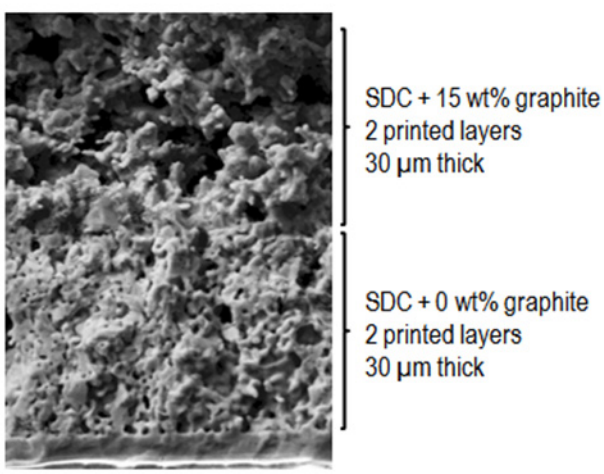

Figure 6. *SDC printed electrode with functionally graded porosity*

Structured Electrodes

In the case of a fuel cell electrode, high surface area with low tortuosity is desirable for a variety of reasons. For gas flow, low tortuosity allows reactant gases to easily permeate through the full thickness of the porous layer. Likewise, low tortuosity also minimizes both ionic and electronic travel distance through the electrodes. Lastly, cathodes are often fabricated by infiltrating a porous framework with nano-scale catalyst materials to increase the amount of active triple phase boundary length [5]. It is much easier to infiltrate the full depth of a porous cathode layer with low tortuosity.

One of the more interesting techniques being investigated to produce electrodes with high surface area and low tortuosity is known as freeze tape casting [6]. With this technique, particulate suspensions are tape cast over a frozen substrate such that the tape cast thick film freezes. As crystals form, particulate matter is rejected to the grain boundaries. When the resulting frozen thick films are freeze dried, the volume of space formerly occupied by ice crystals becomes void. The freeze cast microstructure has a very pronounced directional effect corresponding to the direction in which the tape is pulled. The resulting porous microstructure resembles a series of elongated slivers and is significantly different from conventional porous materials such as those seen in Figure 6. Whereas the pore structure in Figure 6 has extremely high tortuosity, the freeze tape cast structure has very low tortuosity. The aim of this research is to explore the feasibility of combining the most attractive aspects of the freeze tape cast microstructure with the strengths of DW material printing.

When a viscous paste is extruded through a round orifice, as is the case with the micro-extrusion process considered here, it generally takes on a cylindrical shape that may be less than, approximately equal to, or greater than the orifice diameter depending upon the process parameters being used. If the gap between the orifice and the substrate is less than the bead diameter, then the bead will be "squashed" to a certain extent. By depositing multiple beads on top of each other to create a rib structure, it is possible to create a wall having scallops. The net effect is a wall whose surface area is greater than that of a perfectly vertical wall.

With a perfectly vertical wall, the 2D edge length of each wall side equals h, where h is the layer thickness. With a scalloped wall as illustrated in Figure 7, the scalloped edge length can be calculated as a function of the bead radius (r) and layer thickness (h). With reference to Figure 8, the angle (α) that is swept by the scalloped edge is determined as follows:

$$sin\left({}^{\alpha}/_{2}\right) = {}^{h}/_{2r} \quad (1)$$

$$\alpha = 2\sin^{-1}\left(\frac{h}{2r}\right) \quad (2)$$

Since the circumference of a circle having radius r is πD, the edge length of the scallop swept through an angle α on that circle is:

$$L_S = \frac{\alpha}{360}\pi D = \frac{\sin^{-1}\left({}^{h}/_{2r}\right)\pi D}{180} \quad (3)$$

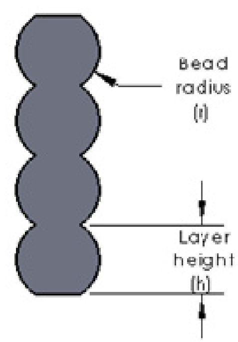

Figure 7. *Printed layers forming a rib*

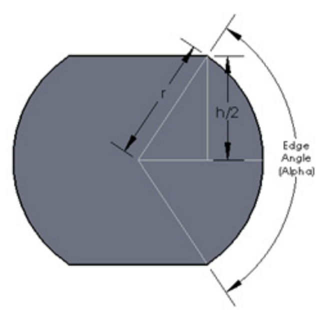

Figure 8. *Printed bead parameters*

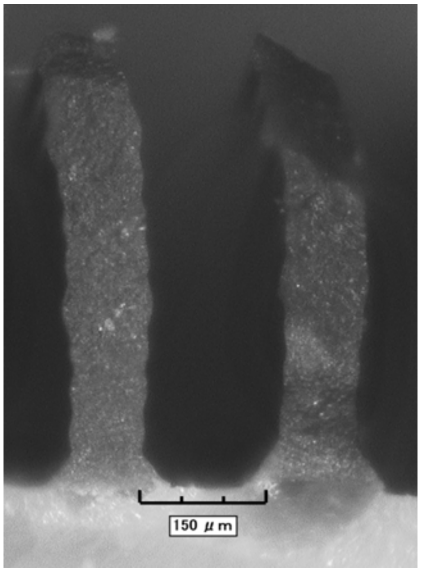

Figure 9. *High aspect ratio Ni-YSZ fins with minimal scalloping*

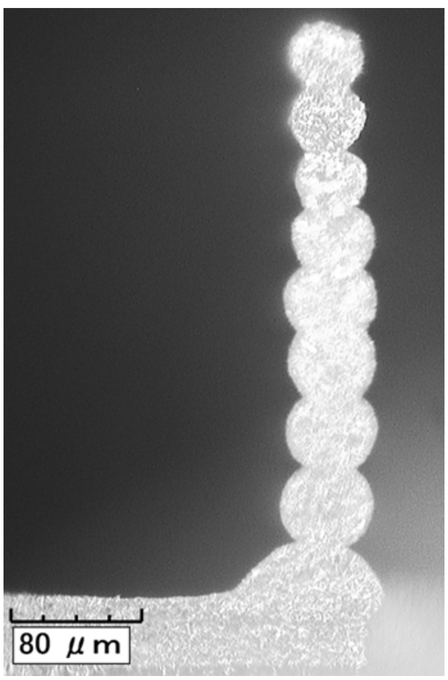

Figure 10. *High aspect ratio Ni-YSZ fins with pronounced scalloping*

If the scallop edge length is compared with a vertical wall edge length of *h*, then the percent increase in edge length, and hence surface area, grows rapidly as the layer height increases relative to a given bead radius. Since surface area is simply edge length multiplied by the length of the rib, the increase in overall electrode surface area scales directly with the increase in edge length. Note that this increase in surface area is achieved with very little adverse influence on the tortuosity of the electrode.

To determine the feasibility of printing extremely high aspect ratio and closely spaced fins with possible applications in SOFC electrodes having low tortuosity, highly viscous pastes were

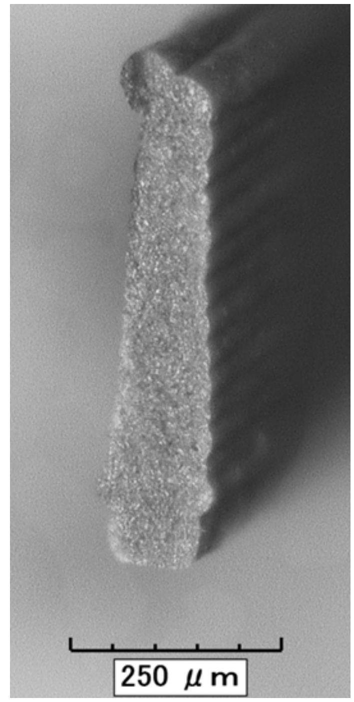

Figure 11. *High aspect ratio Ni-YSZ fins exhibiting some slumping*

formulated in the ratio of 12 grams Ni-YSZ powder to 3ml terpineol-based ink vehicle (Fuel Cell Materials) for the fin shown in Figure 9. The fins shown in Figure 10 and 11 included an additional 0.5 grams (4 wt.%) of graphite powder to further increase the viscosity to the point where extruded beads would hold their shape. Figures 9-12 were all obtained using a Hirox KH-7700 optical microscope equipped with an MGX-2500REZ lens.

Figure 9 illustrates fins with nearly vertical side walls (i.e. almost no "scallop" effect). These ribs were produced by extruding ink at 40 psi through a 125 µm ID ceramic tip with a translation speed of 2.0 mm/sec. A total of 11 layers were printed with each layer having a thickness of 60 µm.

Figure 10 shows a fin structure printed in 9 successive passes through a 75 µm ID ceramic tip. It was printed at 46 psi with a translation speed of 0.75 mm/sec. The average scallop radius following sintering was measured to be 46.5 µm ± 5.5 µm. An average layer height of 36.4 µm ± 4.8 µm was measured following sintering. Plugging these values into Eq. (3) for calculating the edge length, this printed fin has 14.86% more surface area than a smooth walled vertical fin such as the one shown in Figure 9.

Figure 11 demonstrates a tapered rib. It was printed using the exact same ink and process parameters as the fin shown in Figure 10. The layer thickness was 58.90 µm for the first layer and was decreased by 0.05 µm for each successive layer deposited. The reason for this slight reduction in layer thickness with each passing layer is simple. Although the paste being extruded has very high viscosity, it does slump a small amount under the weight of each additional layer deposited (i.e. the rib is noticeably wider at the base, and the scalloping is less visible).

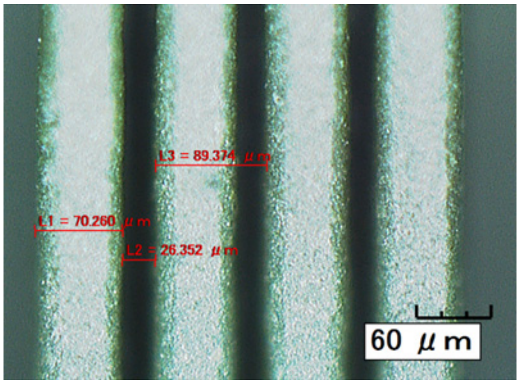

***Figure 12**. Closely spaced Ni-YSZ ribs*

Figures 9-11 demonstrate the ability of this process to generate ribs with extremely high aspect ratios. In order to make this useful in the fabrication of SOFC's, it is necessary to fit as many fins as possible into a given space in order to maximize the total surface area while maintaining extremely low tortuosity. Figure 12 shows a top-down view of ribs printed using a 75 µm nozzle and a 90 µm step-over distance from one track to the next. Following sintering, the rib widths range from approximately 60-70 µm wide, and the channel between each rib is approximately 20-30 µm wide. After being heated in a reducing atmosphere, the NiO in the ribs will reduce to Ni, thus generating a significant degree of porosity (and surface area) within the ribs themselves.

One of the challenges associated with freeze tape casting and the structure shown in Figure 12 has to do with the pronounced directionality of ice crystals and resulting voids in the pore structure. When the elongated pores all align in the same direction, the resulting structure can exhibit significant directional shrinkage stress and warping during sintering. Likewise, the sintered structure is very delicate in the direction orthogonal to the rib orientation. Concentric circles will generate symmetric shrinkage stresses. Having all ribs/channels oriented in the same direction will generate very large stresses along the length of the rib and will also generate a very fragile structure across the direction of ribs. Figure 13 illustrates how the DW micro-extrusion technique can be used to produce a channeled electrode structure whose symmetry evenly balances out shrinkage stresses during sintering.

Conclusions

This paper has introduced the use of a micro-extrusion based direct-write material printing technique to produce solid oxide fuel cell anode and cathode layers. Conventional synthesis techniques such as tape casting and screen printing are very well suited for high volume low cost production. However, there are limits to their flexibility in terms of the extent to which the composition and/or structure of the fuel cells can be spatially controlled in order to improve electrochemical performance.

The feasibility of grading the porosity of electrode layers has been demonstrated, and the possibility of grading porosity within a layer has been discussed. One technical challenge associated with the grading of porosity levels is that the magnitude of shrinkage is influenced by the volume fraction of pore former within the electrode layer. Although the graded porosity has been accomplished by numerous researchers by varying the amount of pore former, a more recent technique involving freeze tape casting also considerable promise. The freeze tape casting method produces a high surface area electrode layer, but one that has very low tortuosity.

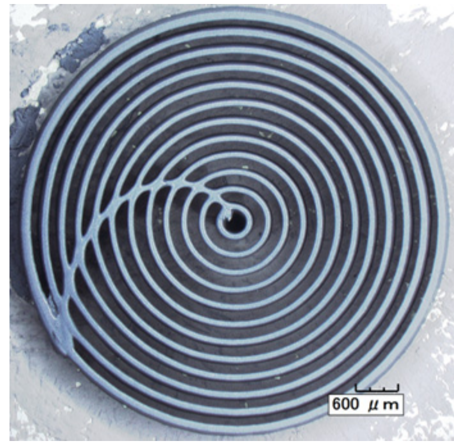

***Figure 13**. Symmetric SOFC channel anode structure*

In this paper, the use of direct-write printing to produce channeled electrodes with arbitrarily complex geometric structures has been demonstrated. A significant advantage of this approach is that symmetric geometries that balance shrinkage stresses and improve mechanical strength can be produced. In future work, the aim is to continue to push the limit on feature size and spacing with this method while also grading the material composition.

Acknowledgement

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Author Biographies

Prasanna Khatri-Chhetri received his BS in Microelectronics Engineering from the Rochester Institute of Technology (2005). He is currently pursuing his MS in Industrial Engineering from RIT where he is studying the use of direct-write printing to produce solid oxide fuel cell electrodes with engineered structure.

Dr. Denis Cormier received his BS in Systems Engineering from the University of Pennsylvania (1989), his MS in Industrial Engineering from the State University of NY Buffalo (1991) and his PhD in Industrial Engineering from North Carolina State University (1995). He is currently holds the Brinkman Professor chair in Industrial and Systems Engineering at the Rochester Institute of Technology where his work focuses on the development of additive manufacturing materials, processes, and applications.

Dr. Fanglin (Frank) Chen received his BS in Chemistry from Anhui University (1992), his MS in Materials Science and Engineering from the University of Science and Technology of China (1995) and his PhD in Materials Science and Engineering from Georgia Institute of Technology (2001). He is currently an assistant professor of Mechanical Engineering at the University of South Carolina where his research interests include synthesis and characterization of materials for energy conversion and storage.

Dr. Prasun Majumdar received his BS in Mechanical Engineering from Bangladesh University of Engineering & Technology (1999), his MS in Mechanical Engineering from Tuskegee University (2004) and his PhD in Engineering Science and Mechanics from Virginia Polytechnic Institute (2008). He is currently an assistant professor of Mechanical Engineering at the University of South Carolina where his research interests include multi-physics analysis of heterogeneous material systems.