Laser 3-D Printing of Highly Compacted Protonic Ceramic Electrolyzer Stack

Jianhua "Joshua" Tong (Primary Contact), Kyle S. Brinkman, Fei Peng, and Hai Xiao
Clemson University
515 Calhoun Drive
Clemson, SC 29634
Phone: 864-655-4954
Email: jianhut@clemson.edu

DOE Manager: Brian Hunter
Phone: 240-562-1347
Email: Brian.Hunter@ee.doe.gov

Contract No.: DE-EE0008428

Project Start Date: November 6, 2019
Project End Date: April 30, 2021 (the no-cost extension was done for Budget Period 1)

Overall Objectives

- Develop compatible high-performance intermediate temperature protonic ceramic electrolyzer stack (IT-PCES) component materials, printable component pastes, and rapid laser reactive sintering (RLRS) technology.
- Manufacture large-area, high-performance, and stable IT-PCESs by laser 3-D printing (L3DP) technology.
- Complete initial techno-economic analysis for hydrogen production in IT-PCES and show significant cost decrease compared to state-of-the-art electrolyzers at the same production scale.
- Demonstrate the commercial viability of IT-PCES manufactured by L3DP technology by boosting the technology readiness level to >4.

Fiscal Year (FY) 2019 Objectives

- Discover PCES component materials of electrolyte, hydrogen, and oxygen electrodes and interconnect with high performance and excellent compatibility.
- Achieve the precursor pastes compositions, 3-D printing parameters, and RLRS conditions for manufacturing crack-free component layers with controlled thickness, configuration, and microstructure.
- Solve the challenges of binding between component layers and infiltration in porous electrode scaffolds and manufacture PCES single cells by L3DP technique.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan[1]:

- **Capital Cost:** Capital cost of water electrolysis system is prohibitive to widespread adoption.
- **System Efficiency and Electricity Cost**: Low-cost cell stacks addressing efficiency are needed.
- **Manufacturing**: Electrolysis units are produced in low volume. The fabrication technology is highly capital intensive.

Technical Targets

This project includes two one-year budget periods. During Budget Period 1, PCES single cells will be manufactured by L3DP and tested. Budget Period 1 will address the following:

- Milestone 1.1: Discovery of new PCES materials (discover compatible electrolyte, O_2/H_2 electrodes, and interconnect with low area specific resistance [ASR]).
- Milestone 1.2: High materials performance in PCES single cells from selected materials fabricated by solid state reactive sintering.
- Milestone 2.1: 3-D printing of component large-area, crack-free green films.
- Milestone 2.2: RLRS of component large-area crack-free thin films.

[1] https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22

- Milestone 3.1: Effective binding of PCES component films.
- Milestone 3.2 Effective infiltration in the L3DP electrode nanoparticles showing oxygen evolution reaction and hydrogen evolution reaction.
- Milestone 3.3: Demonstrate high-performance PCES single-cell fabrication by L3DP.
- Milestone 3.4: The rough order of magnitude calculation to show the L3DP has the potential to offer a lower cost than conventional technologies.

FY 2019 Accomplishments

- The performance of the Ni-BCZYSm10 | BCZYSm10 | BCZY63-BCFZY0.1 single-cell-based newly discovered $BaCe_{0.7}Zr_{0.1}Y_{0.1}Sm_{0.1}O_{3-\delta}$ (BCZYSm10) fabricated by solid state reactive sintering method showed a peak power density of 410 mW/cm^2 at 600°C in fuel cell mode and a current density 370 mA/cm^2 at 1.3 V and 600°C in electrolysis cell mode.
- A new triple-conducting $BaCe_{0.4}Fe_{0.4}Co_{0.2}O_{3-\delta}$ (BCFC) nanocomposite O_2 electrode was discovered, which showed an ASR ~0.075 Ω·cm^2 and peak power density of ~335 mW/cm^2 at 700°C.
- The phase-pure and fully dense interconnect of $La_{0.7}Sr_{0.3}CrO_3$ (LSCr) was fabricated by a rapid laser reactive sintering method, which showed better phase purity and microstructure than traditional furnace sintering.
- The rapid laser reactive sintering achieved desired crystal phases and microstructure (dense and porous) for protonic ceramic-based electrolytes, H_2 electrodes, O_2 electrodes, and interconnects.
- The pastes for model component (electrolyte, H_2 electrode, O_2 electrode, and interconnect) precursor mixtures were prepared, and the defect-free homogenous component layers with active area >100 cm^2 were printed.
- The crack-free and pore-free BCZYYb + 1 wt % electrolyte film as thin as 20 μm was obtained on reduced half cells by RLRS, which showed more than 60% success rate and active area more than 10 cm^2.
- Porous 40 wt % BCZYYb + 60 wt % NiO H_2 electrode thin films were deposited on inert porous alumina substrate by RLRS.
- The half cells based on porous 40 wt % BCZYYb + 60 wt % NiO H_2 electrode and fully densified BCZYYb + 1 wt % NiO electrolyte with an area >10 cm^2 were obtained by one-step laser processing.
- The single cells based on porous 40 wt % BCZYYb + 60 wt % NiO H_2 electrode, fully densified BCZYYb + 1 wt % NiO electrolyte, and porous BCZY63 O_2 electrode scaffold fabricated by one-step laser processing, which showed an active area more than 5 cm^2.
- Demonstrated that the updated 3-D printing technique based on microextrusion and Dr. Blade smoothing can achieve green films as thin as 50 μm and a perfect area around 12 cm^2, which can strengthen the capability of 3-D printing for manufacturing much thinner ceramic films.
- The half cells comprised of 40 wt % BCZYYb + 60 wt % NiO H_2 electrode and BCZYYb + 1 wt % NiO were fabricated by L3DP, which showed a total active area >120 cm^2. The individual half cells have a width of ~1 cm and a length longer than 6 cm. The thickness of electrolyte films can be controlled as thin as 10 μm.
- The single cells with half cells fabricated by L3DP showed a peak power density of around 223 mW/cm^2 at 600°C under air/H_2 gradient. The stable operation around 140 h was obtained. The active cell area is about 0.2 cm^2.
- The very rough initial cost estimation of L3DP of PCES showed the manufacturing cost might only count a small percentage.

INTRODUCTION

In FY 2019, Clemson University discovered new oxygen electrode materials and protonic ceramic electrolyte materials, which showed comparable performance with state-of-the-art materials. We demonstrated the microextrusion-based 3-D printing technique could print protonic ceramic electrolyzer component thin films with dimensions larger than 10 x 10 cm^2. The rapid laser reactive sintering technique can be used to achieved fully densified protonic ceramic electrolyte and porous electrodes with active areas larger than 10 cm^2 and desired crystal structures and microstructures. The protonic ceramic single cells manufactured by laser 3-D printing achieved power density higher than 220 mW/cm^2 and stability longer than 140 h at 600°C.

The achievement that Clemson University has made can experimentally prove the proposed concept of laser 3-D printing of protonic ceramic electrolyzer cells is feasible, which contributes to the DOE's mission of providing a cost-effective and efficient manufacturing technique to speed the high-temperature electrolyzer in multiscale.

APPROACH

Develop intermediate temperature protonic ceramic electrolyzer materials and demonstrate suitable water electrolysis and fuel cell performance. The solid state reactive sintering method was used to prepare single cells and half cells. The electrochemical impedance spectroscopy was used to characterize the material performance. The approach addresses barriers (F) capital cost and (G) system efficiency by improving electrolyzer power density and durability at lower temperatures (e.g., 600°C).

Develop laser 3-D printing to achieve high-quality component films and protonic ceramic electrolyzer single cells. The 3-D printing based microextrusion was used to print the component layers of protonic ceramic electrolyzer stack, half cells, and single cells. The CO_2 lasers with point beam and cylindrical beams were used to prepare thin films of PCES components and half cells and single cells.

RESULTS

In FY 2019, we discovered new protonic ceramic material of BCZYSm10 and fabricated PCES single cells by solid state reactive sintering method with BCZYSm10 as the electrolyte, 40 wt % BCZYSm10 + 60 wt % NiO as H_2 electrode, BCZY63 as O_2 electrode scaffold, and BCFZY0.1 as O_2 electrode active phase. The single cells with an electrolyte layer thickness of about 25 μm were measured for both fuel cell and electrolysis cell performance. The electrochemical impedance spectroscopy measurement showed that the ASR of the electrolyte was ~0.34 $\Omega \cdot cm^2$ at 600°C. The sum ASR of the H_2 and O_2 electrodes was about 0.14 $\Omega \cdot cm^2$ at 600°C, which already met our milestone (0.2 $\Omega \cdot cm^2$ at 600°C).

Figure 1 provides the single-cell performance for the operation in both fuel cell and electrolysis cell modes. The I-V curves in the solid oxide fuel cell (SOFC) were obtained down to 0.5 V, which is enough to reach the maximum power density of the cell (P_{max}) at each temperature. The P_{max} value reaches 410 mW/cm^2 at 600°C. The further enhancement of output characteristic can be realized through the optimization of electrode microstructures and electrolyte thin film development. The I-V curves in the solid oxide electrolysis cell (SOEC) mode of operation was obtained, with 12 vol % H_2O humidified air as feed gas and 5% H_2 as the sweep gas. The cell was also able to produce a current density of 370 mA/cm^2 at 1.3 V at 600°C. The developed cell operating in the SOEC mode possesses encouraging performance in comparison with most of the previously studied systems. It is worth mention that the electrolysis performance can be further enhanced by increasing the water content in the feed stream.

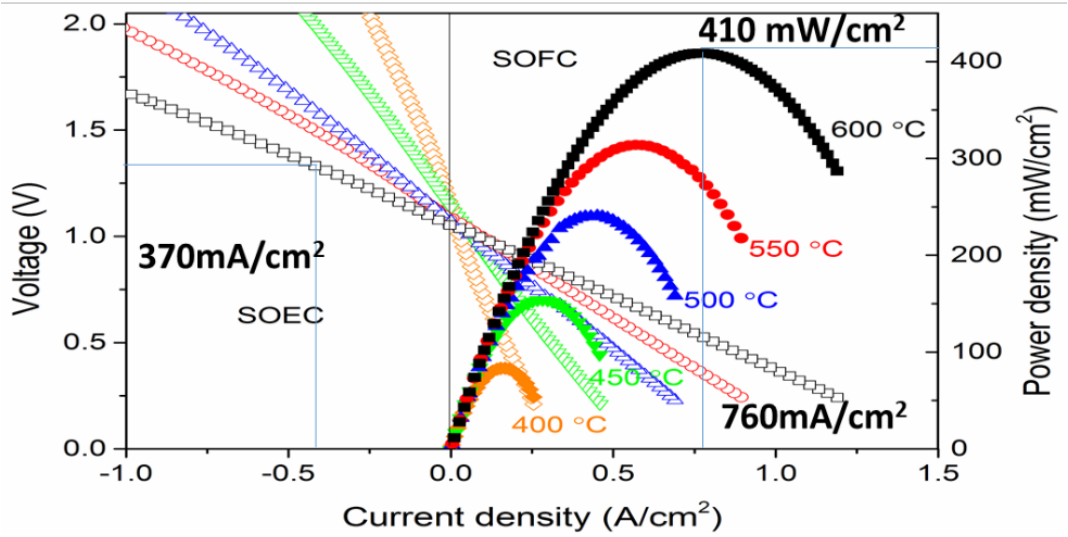

Figure 1. I-V curves and corresponding power densities of 40 wt % BCZYSm10 + 60 wt % NiO | BCZYSm10 + 0.25 wt % Fe_2O_3 | BCZY63 + BCFZY0.1 cell at 400°–600°C under SOFC working mode under H_2/air atmosphere, and electrolysis performance measured under 12 vol % H_2O humidified air/5% H_2 (cathode area: 0.38 cm^2)

In FY 2019, we developed paste recipe and improved the microextrusion-based 3-D printing technique for printing PCES component films, half cells, and single cells. We prepared high-quality BCZYYb + 1 wt % NiO electrolyte, 40 wt % BCZYYb + 60 wt % NiO H_2 electrode, BCFZY0.1 O_2 electrode, and LSCr interconnect pastes. By using our microextrusion method, we can easily print green films with thicknesses around 150–1,000 µm for all four components. All four component precursor green films were successfully printed, with active areas higher than 100 cm^2 and very smooth surface. These results already met our milestone request (100 cm^2 for green component films). Figure 2a shows that the three layers of H_2 electrode, electrolyte, and O_2 electrode were bonded together very well. Figure 2b shows a representative cross-sectional image of electrolyte green film printed on H_2 electrode film. The excellent bonding between the electrolyte film and the H_2 electrode film was achieved for 3-D printed green half cells.

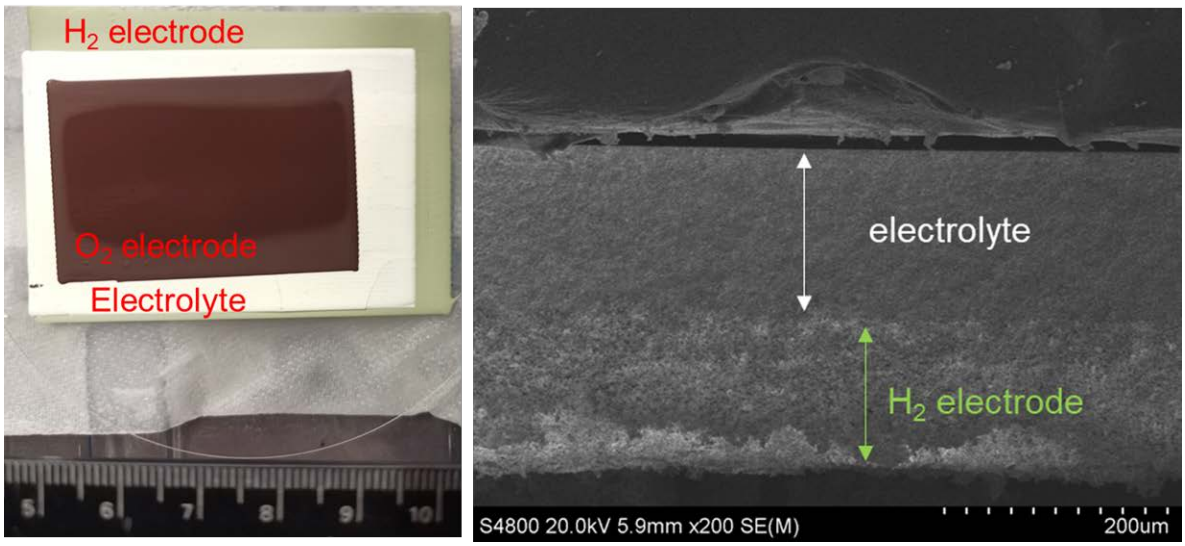

Figure 2. (a) Three layers of H_2 electrode, electrolyte, and O_2 electrode printed by microextrusion-based 3-D printing technique and (b) scanning electron microscopy (SEM) image of two-layer cross-section (electrode green film on H_2 electrode green film)

In FY 2019, we developed an RLRS technique based on a cylindrical lens, which allows the line scan of the green films. Based on this technique, by optimizing laser operating parameters, paste properties, and thin-film thickness, the protonic electrolyte, H_2 electrode, and H_2 electrode supported electrolyte half cells with active area larger than 10 cm^2 were prepared by RLRS. The electrolyte layer with thickness 10–50 μm supported on porous O_2 electrodes was obtained. The green half cells having a much larger area than the width of the laser beam through the cylindrical lens always resulted in the sintered stripes separated from the region without sintering. The discrete laser beam distribution resulted in a discrete edge effect. Therefore, we removed the edge effect by printing half cells in a narrow width in the dog bone shape. The 3-D printing, spray coating, and RLRS conditions are the same as the ones for preparing half cells of 100@200 sample except that the dog-bone shaped cells were used. Figure 3 provides a summary photo of 13 half cells, which has a total active area around 120 cm^2. The preparation of this amount of half cells allows us to further integrate them into large-area cells or stacks, which is significant progress on this project.

Figure 3. Summary optical photo of half cells fabricated by L3DP

In FY 2019, the half cells comprised of 40 wt % BCZYYb + 60 wt % NiO H_2 electrode and BCZYYb + 1 wt % NiO electrolyte strips were prepared by 3-D printing followed by one-step RLRS (60 w laser power, 15 mm defocus, and 0.1 mm/s laser scan speed). The strips were cut into multiple circular half cells by picosecond laser, which was further coated BCFZY O_2 electrode layer by conventional screen printing followed by annealing at 900°C for 2h. Figure 4a shows the optical photo of the single cells after the coating of BCFZY0.1 O_2 electrodes. Figure 4b, the SEM image of the fracture cross-section of the single cells**,** indicates that both H_2 electrode and O_2 electrode are very porous. The electrolyte film is sufficiently dense and has a thickness of around 7 μm. The thickness of the O_2 electrode is around 4.0 μm.

The I-V and I-P curves of these single cells at different temperatures are shown in Figure 4c. The open-circuit voltages of the cell were 1.06 V, 1.03 V, and 0.99 V at 550°C, 600°C, and 650°C, respectively, and the corresponding maximum power densities were 153, 223, and 287 mW/cm^2. Figure 4d shows the ASRs versus operating temperatures. As the temperature increased from 550°C to 650°C, the total resistance of the single cell (R_t) decreased from 1.77 to 0.75$\Omega \cdot cm^2$, and the electrolyte resistance (R_o) decreased from 0.45 to 0.22$\Omega \cdot cm^2$.The peak power density increased with temperature from 550°C to 650°C. Figure 4e provides the long-term test of the stability of the single cells. The operation of ~140 hours at peak power density at 600°C is relatively stable.

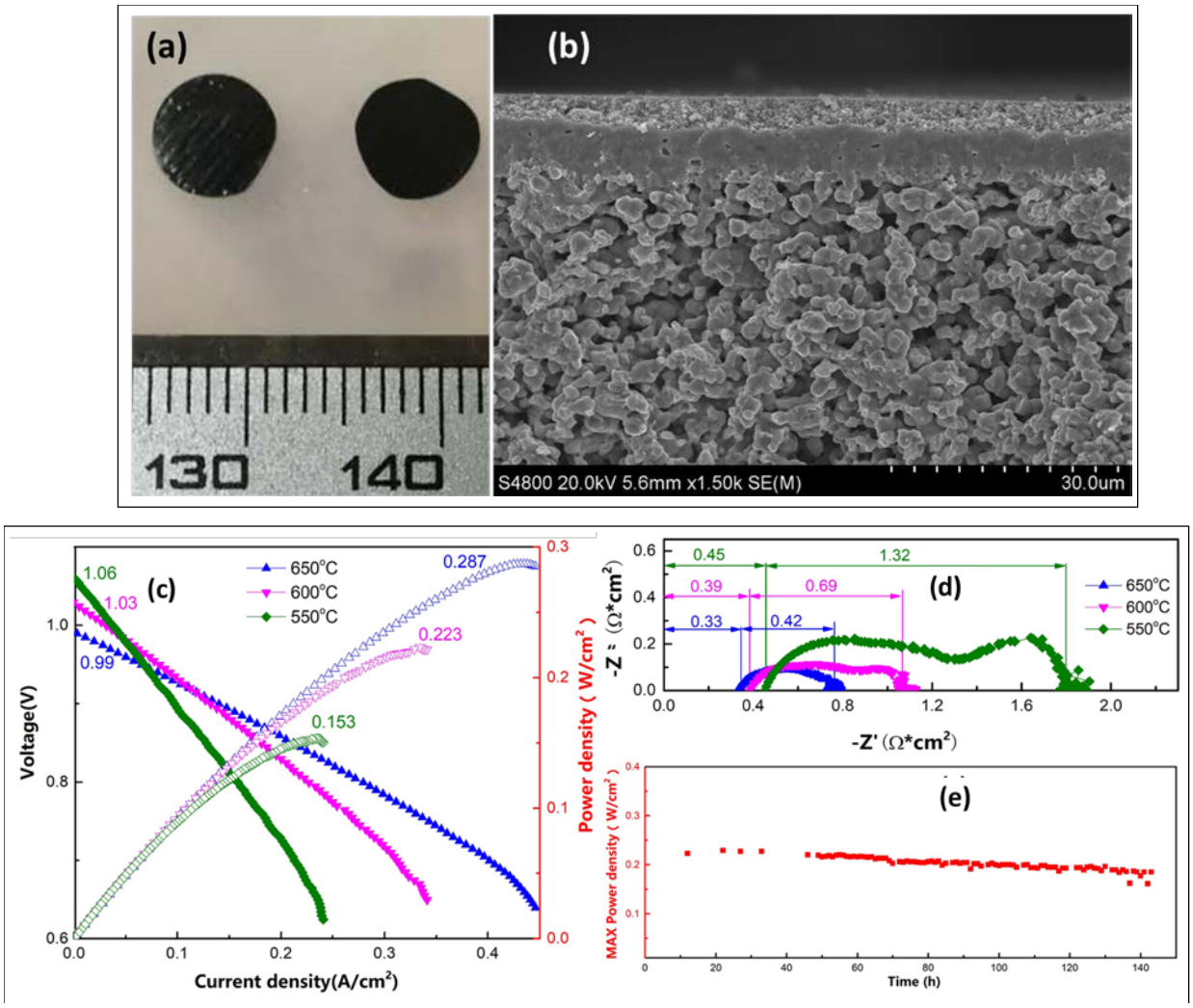

Figure 4. (a) Optical photo of single cell and (b) SEM image of the cross-section of single cells. (c) I-V and I-P curves of the single cells with half cells fabricated by 3-D printing followed by RLRS, (d) electrochemical impedance spectroscopy spectra of the single cells under open circuit condition, and (e) long-term stability test.

CONCLUSIONS AND UPCOMING ACTIVITIES

- Continue to discover PCES component materials to achieve of 1000 mA/cm^2 at 1.3 V and 600°C for electrolysis operation.
- Solve the bonding problem between the sintered component layer and the next component for successfully operating RLRS.
- Successfully do infiltration of electrode active phase to meet the ASR target for both electrodes.
- Decrease the electrolyte thickness and optimize the microstructure and composition to achieve ohmic resistance lower than 0.1 Ω·cm^2.
- Fabricate single cells by laser 3-D printing technique with active area more extensive than 5 cm^2, current density higher than 500 mA/cm^2, and stability longer than 500°C.
- Demonstrate PCES single cells with area >5 cm^2, current density >500 mA/cm^2 at 1.3 V, and stable operation with a degradation rate <1% for >200 h at 600°C by L3DP.

- Obtain the interconnects with designed microchannels, which should show negligible mass transport resistance and no deterioration to current collecting performance.
- Achieve program to control L3DP to manufacture designed PCES.
- PCES with cells >5 and area >100 cm^2 will be manufactured by the proposed L3DP technology. The PCES will have a current density >1 A/cm^2 at 1.3 V and degradation rate <1% per 1,000 h at 600°C
- The models for estimating the electrolyzer manufacturing cost by L3DP technology will be established for predicting hydrogen cost by H2A3. The key parameters for further decreasing hydrogen cost to meet DOE's target of \$2/kg H_2 will be identified.
- To speed up the technology to market, an industrial partner who is interested in scaling up this technology will be located. A reasonable scale-up plan will be made.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. "Laser 3D Printing of Highly Compacted Protonic Ceramic Electrolyzer Stack," Quarter 1, 2, and 3 reports in FY 2019.
2. Yuqing Meng, Jun Gao, Jack Duffy, Jianhua Tong, and Kyle S. Brinkman, "A High-Performance Reversible Protonic Ceramic Electrochemical Cell based on a Novel Sm-Doped $BaCe_{0.7}Zr_{0.1}Y0.2O_3$ Electrolyte," *Journal of Power Sources* 440 (2019): 227122.
3. J. Tong, "Rapid Laser Reactive Sintering for Protonic Ceramic Electrochemical Cells," Invited Talk, O-HyLi: Frontiers in Convergent Research in Energy and Informatics, Northwestern University, Evanston, IL, September 3–5, 2019.
4. Jianhua "Joshua" Tong, Shenglong Mu, Hua Huang, Yuqing Meng, Yuzhe Hong, Minda Zou, Jincheng Lei, Jack Duffy, Zeyu Zhao, Xiao Geng, Fei Peng, Kyle Brinkman, and Hai Xiao, "Laser 3D Printing of Protonic Ceramic Electrochemical Devices," 22nd International Conference on Solid State Ionics (SSI-22), Pyeong chang-Gun Gangwon-Do, Korea, June 16–21, 2019,.
5. J. Tong, Z. Zhao, S. Mu, and M. Zou, "Triple Conducting Perovskite Oxide Nanocomposites as Oxygen Electrodes for Intermediate-Temperature Protonic Ceramic Cell," 235th ECS Meeting, Dallas, TX, May 26–30, 2019.
6. S. Mu, Y. Hong, J. Lei, Y. Song, Z. Zhao, D. Jiang, F. Peng, H. Xiao, and J. Tong, "Protonic Ceramic Electrochemical Devices by Integrated 3D Printing and Laser Processing," Electronic Materials and Applications 2019 (EMA2019), Orlando, FL, January 23–25, 2019.