Laser 3D Printing of Highly Compacted Protonic Ceramic Electrolyzer Stack

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Clemson University

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Project ID: ta025

Overview

Timeline

- **Project Start Date: 10/01/18***
- **Project End Date: 10/31/20**
- **Budget Period 1: 10/01-10/31/19**
- **Percent Complete (BP1): ~20%**

* Project Actual Start Date is 11/06/18

Budget

- **Total Project Budget: $2M**
- **Total Recipient Share: $400K**
- **Total Federal Share: $1.6M**
- **Total DOE Funds Spent*: $45,443.81**
- **Total Recipient Funds Spent*: $19,274.62**

* As of 3/01/19

Barriers

– **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. Fabrication technology is high capital intensive.

Partners

- **Clemson is the sole award recipient**
- **Industrial board is being established**
- **Clemson is interested in partnering with lab and industrial collaborators**

Relevance

Objectives: This project will design, understand, develop, and demonstrate a laser 3D printing (L3DP) technology for cost-effective, rapid, and flexible manufacturing high-performance intermediate-temperature (IT, 350-650^oC) protonic ceramic electrolyzer stacks (PCESs) for H_2 production at various scales to meet DOE's H_2 production objectives.

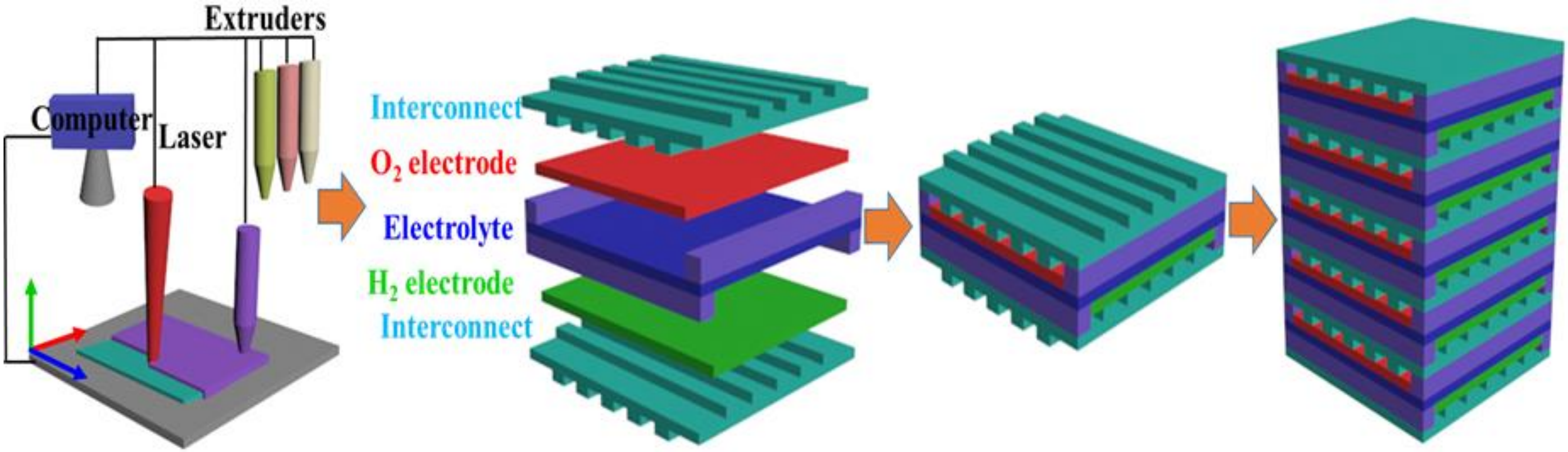
Project Targets: 1) A PCES composed of >5 single cells with total area >100cm^2 will be manufactured by the L3DP technology. **2)** The current density >1A/cm^2 at 1.3 V and degradation rate <1% per 1000h at 600^oC will be achieved. **3)** The H_2 cost based on the initial TEA should decrease >50% compared to the state-of-the-art electrolyzers and show the trend to be close to $2/kg. **4)** The TRL will be boosted to >4 and the potential industrial partner will be found and scale-up plan should be made.

Budget Period 1 Target: 1) PCES single cells with area >5cm^2, current density >500mA/cm^2 at 1.3V and stable operation with degradation rate <1% for >200h at 600^oC by L3DP. **2)** The rough order of magnitude calculation will show the potential for the L3DP technology to be cost incentive comparing to conventional technologies.

Approach

1. **PCES Materials Development**
2. **PCES Component Thin Films by L3DP**
3. **PCES Single Cells by L3DP**
4. **Five-Cell PCES by L3DP**
5. **Initial TEA and Market Transformation Plan**

PCES, protonic ceramic electrolyzer stack
L3DP, laser 3D printing



Approach-**BP1**

1. Develop intermediate temperature protonic ceramic electrolyzer materials and demonstrate good water electrolysis and fuel cell performance.

Address barriers: F capital cost and G system efficiency by improving electrolyzer power density and durability at lower temperatures (e.g., 600^{o}C).

2. Laser 3D print high-quality component films and protonic ceramic electrolyzer single cells.

Address barriers: F, capital cost, G. System efficiency, K manufacturing by rapidly, digitally, and cost-effectively fabricating protonic ceramic electrolyzer with high volumetric power density.

Manufacturing of cost-effective electrolyzers for H_2 production through H_2 electrolysis at various scales.

Approach

Approach-Milestone

Budget Period 1: Protonic Ceramic Electrolyzer Single Cells by Laser 3D Printing

Task #	Milestones	Task Completion Date	
		Planned	% Complete
1.1	Discovery of new PCES materials (Discover compatible electrolyte, O_2/H_2 electrodes, and interconnect with low ASRs)	8/31/19	30%
1.2	High materials performance in PCES single cells from selected materials fabricated by solid state reactive sintering	8/31/2019	25%
2.1	3D printing of component large-area, crack-free green films	8/31/2019	25%
2.2	Rapid laser reactive sintering (RLRS) of component large-area crack-free thin films	8/31/2019	25%
3.1	Effective binding of PCES component films	10/31/2019	10%
3.2	Effective infiltration in the L3DP electrode nanoparticles showing OER and HER	10/31/2019	10%
3.3	Demonstrate high-performance PCES single cell fabrication by L3DP	10/31/2019	10%
3.4	The rough order of magnitude calculation to show the L3DP has potential to offer lower cost than conventional technologies	10/31/2019	5%
GNG	Demonstrate PCES single cells with area >5cm^2, current density >500mA/cm^2 at 1.3V and stable operation with a degradatio rate <1% fo >200h at 600°C by L3DP	10/31/2019	20%

Accomplishments and Progress

Task-1 PCES Materials Development

- **The new electrolyte material of BCZYS was discovered with a total conductivity near to 2x10-2 $\Omega^{-1}\cdot cm^{-1}$.**
- **The new triple conducting BCF nanocomposite cathode was discovered, which showed an area specific resistance (ASR) ~0.3 $\Omega\cdot cm^2$ at 600^oC based on symmetrical cell measurement with $BaCe_{0.7}Zr_{0.1}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BCZYYb) as the electrolyte.**
- **The commonly used interconnect of $La_{0.7}Sr_{0.3}CrO_3$ (LSCr) was synthesized, and the total electrical conductivity of 16.2 S/cm^{-1} was obtained.**
- **The model component materials of BCZYYb + 1wt% NiO electrolyte, 40wt% BCZYYb + 60wt% NiO H_2 electrode, $BaCo_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1}O_{3-\delta}$ (BCFZY0.1) O_2 electrode active phase, $BaCe_{0.6}Zr_{0.3}Y_{0.1}O_3$ (BCZY63) O_2 electrode scaffold, and LSCr interconnect were selected to perform laser sintering for achieving desired microstructures.**

Accomplishments and Progress

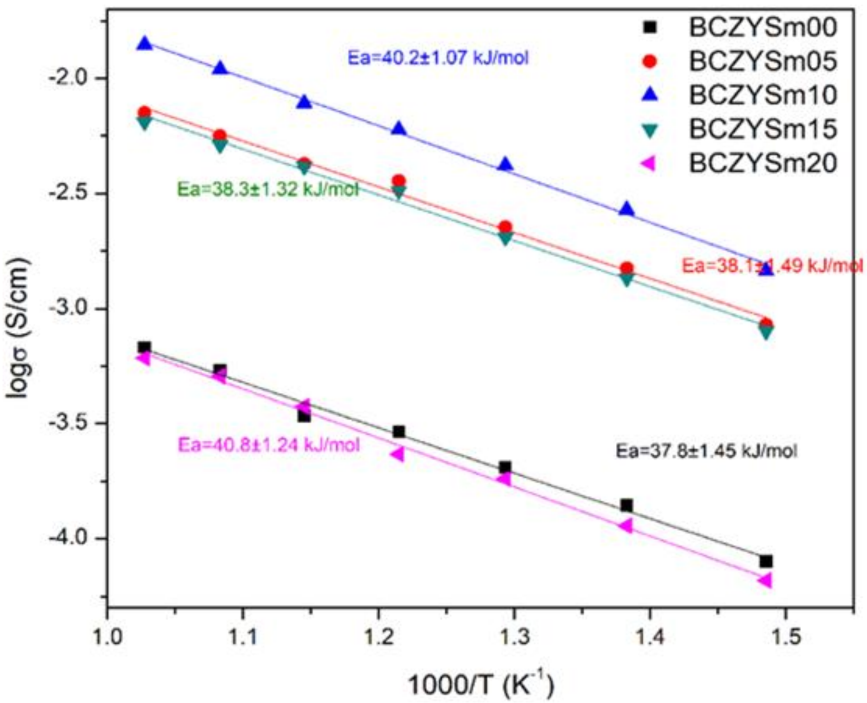
- **The new Ni-BCZYS | BCZYS | BCZY63-BCFZY0.1 single cell obtained by solid state reactive sintering (SSRS) technique showed a peak power density of 313 mW/cm^2 at 600 ^oC and current density 350 mA/cm^2 at 1.3 V and 600 ^oC.**

Task-2 PCES Component Thin Films by L3DP

- **The pastes for model component materials have been prepared for printing defect-free homogenous layers with effective area >30cm^2.**
- **The line laser scan based on a cylindrical lens has been confirmed to be able to achieve fully densified BCZYYb+1wt% NiO electrolyte film on the reduced porous 40wt% BCZYYb + 60wt% NiO H_2 electrode substrates with an area >2 cm^2.**
- **The defect-free porous 40wt% BCZYYb + 60wt% NiO H_2 electrode with an area >2.2 cm^2 were obtained by laser sintering.**
- **The BCFZY0.1 O_2 electrode layers with good porosity and small grain size were obtained by laser processing paste from phase-pure BCFZY0.1 nanoparticle synthesized by a modified Pechini method.**

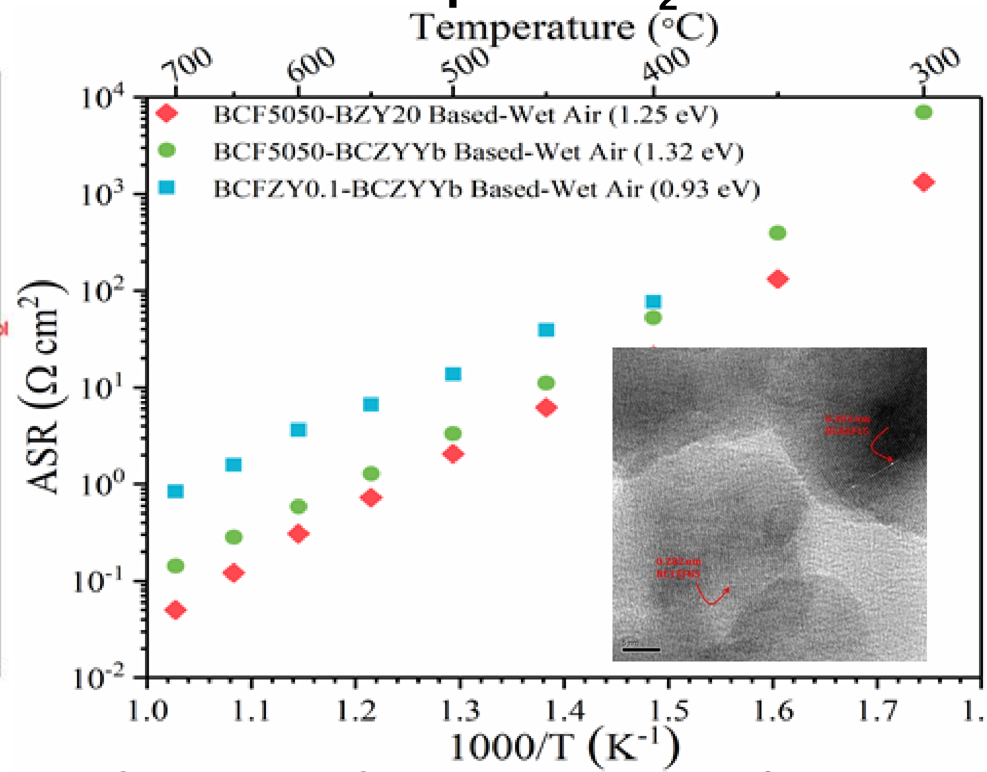
MS1-Discovery of New PCES Materials

New BCZYS Electrolyte



Total conductivity VS temperature in wet 5% H_2

New Nanocomposite O_2 Electrode



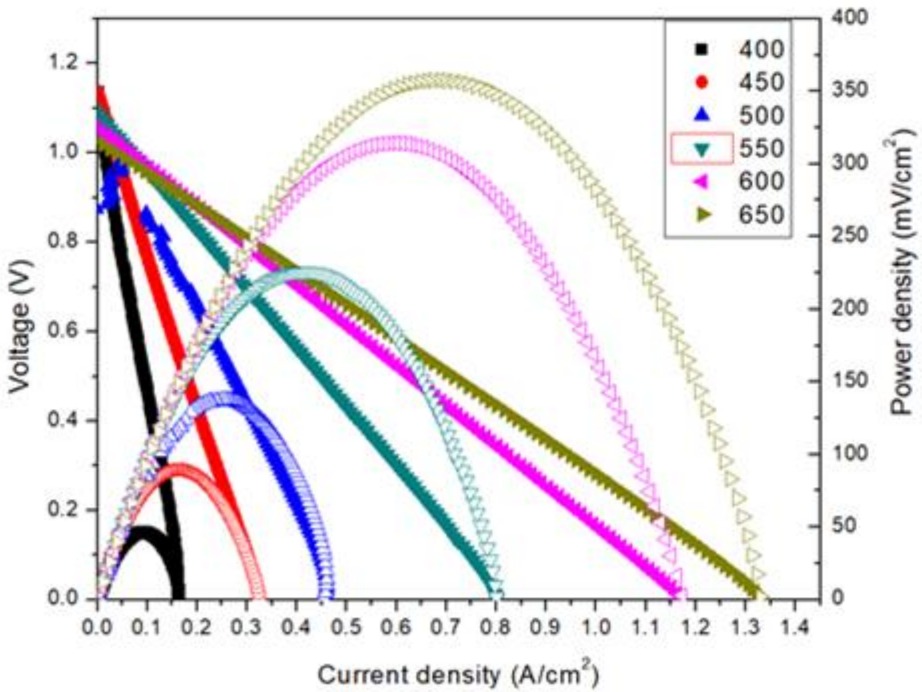
Performance of BCF nanocomposite oxygen electrode based on symmetrical cells.

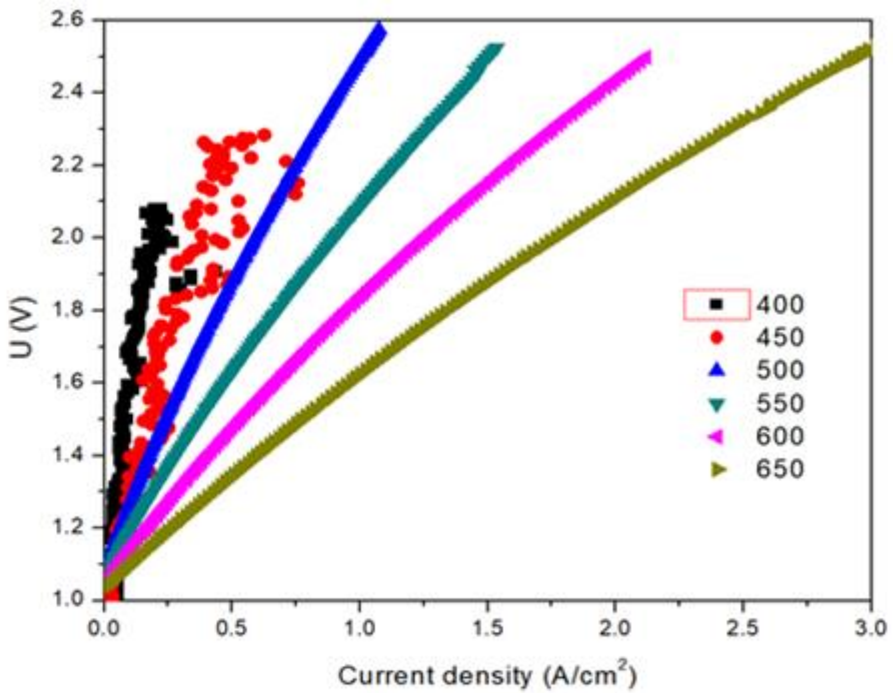
The new electrolyte material of BCZYS was discovered with a total proton conductivity near to **$2x10^{-2}$ $\Omega^{-1}\cdot cm^{-1}$**.

The new triple conducting BCF nanocomposite O_2 electrode was discovered, which showed an **ASR ~0.3 $\Omega\cdot cm^2$ at 600ºC** based on symmetrical cell with $BaCe_{0.7}Zr_{0.1}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BCZYYb) as the electrolyte.

Accomplishment

MS2- Materials Performance in PCES Single Cells

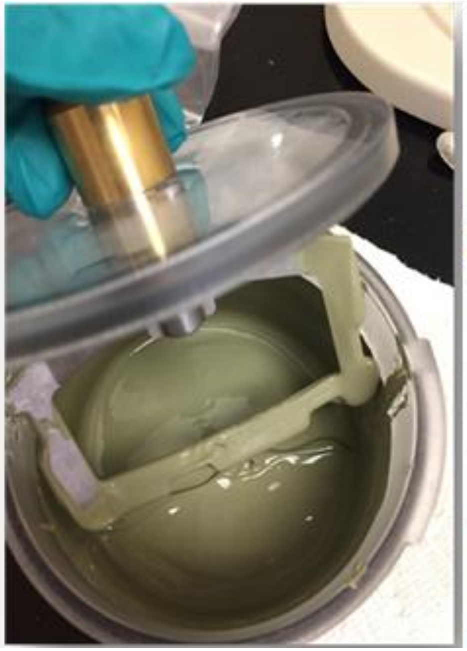


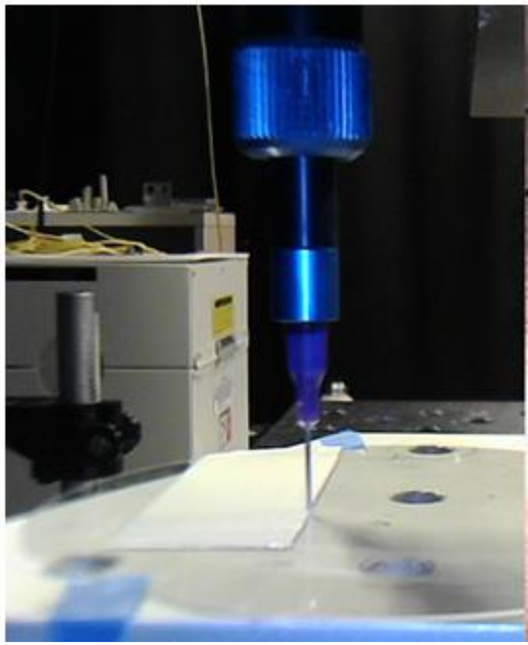


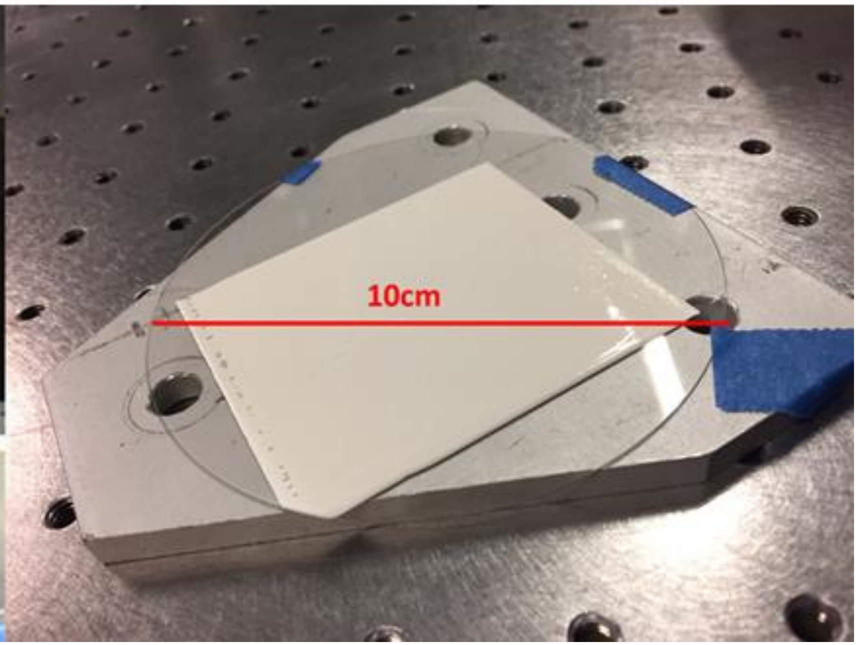
I-V curves and corresponding power densities of 40 wt.% BCZYS+60 wt.% NiO | BCZYS + 1wt% NiO | BCZY63 0.025 wt.% Fe_2O_3 cell at 400 – 650°C under H_2/air (left). I-V curves of SOEC mode measured at 400-650°C under 12 vol.% H_2O humidified air/5% H_2 (right).

The new Ni-BCZYS | BCZYS | BCZY63-BCFZY0.1 single cell obtained by solid state reactive sintering (SSRS) technique showed a peak power density of **313 mW/cm² at 600 °C** and current **density 350 mA/cm² at 1.3 V and 600°C.**

MS3-3D Printing of Component Green Films







Printable BCZYYb + 1wt% NiO paste.

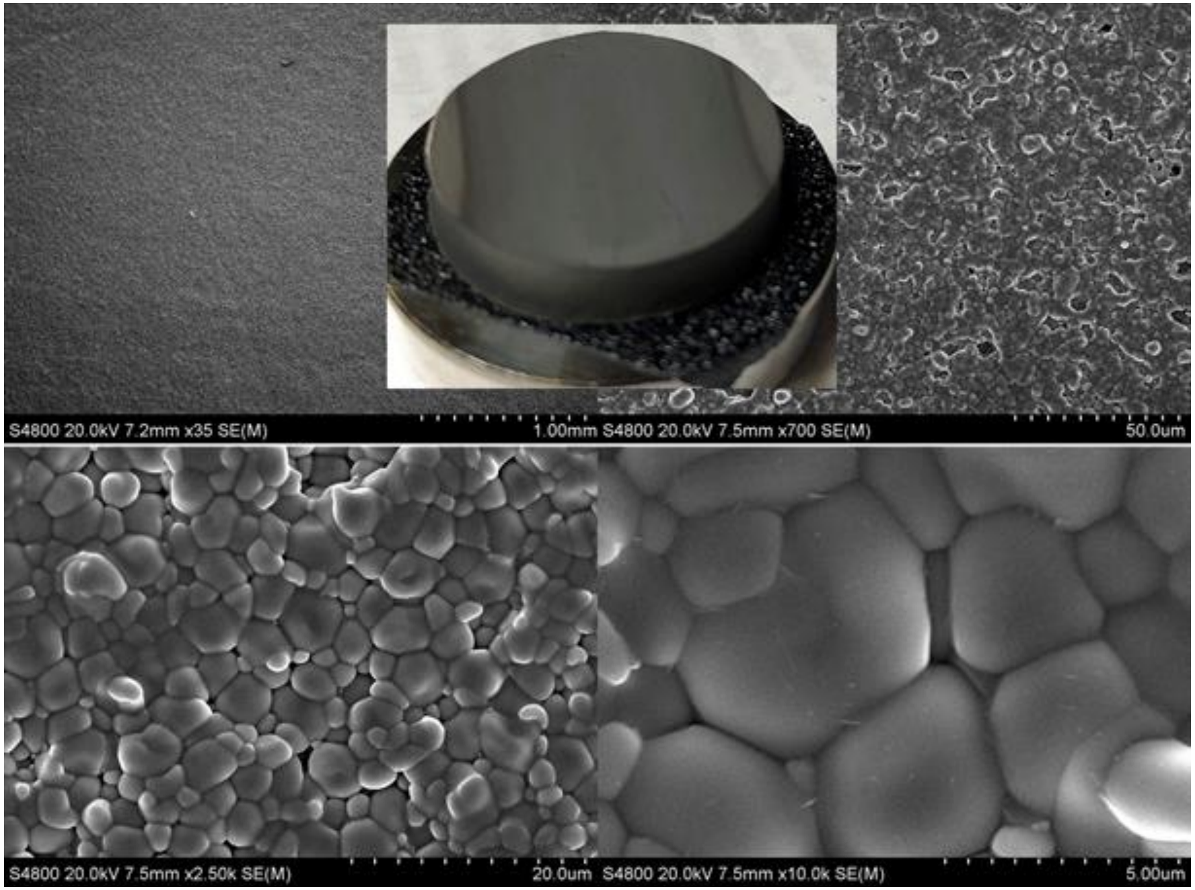
Photo of 3D printing green film by microextruder (middle) and BCZYYb+1wt% NiO green films fabricated by 3D printing based on microextrusion technique (right).

The pastes for model component materials have been prepared for printing defect-free homogenous layers with effective area **>30cm²**.

Accomplishment

MS4-RLRS of Component Thin Films

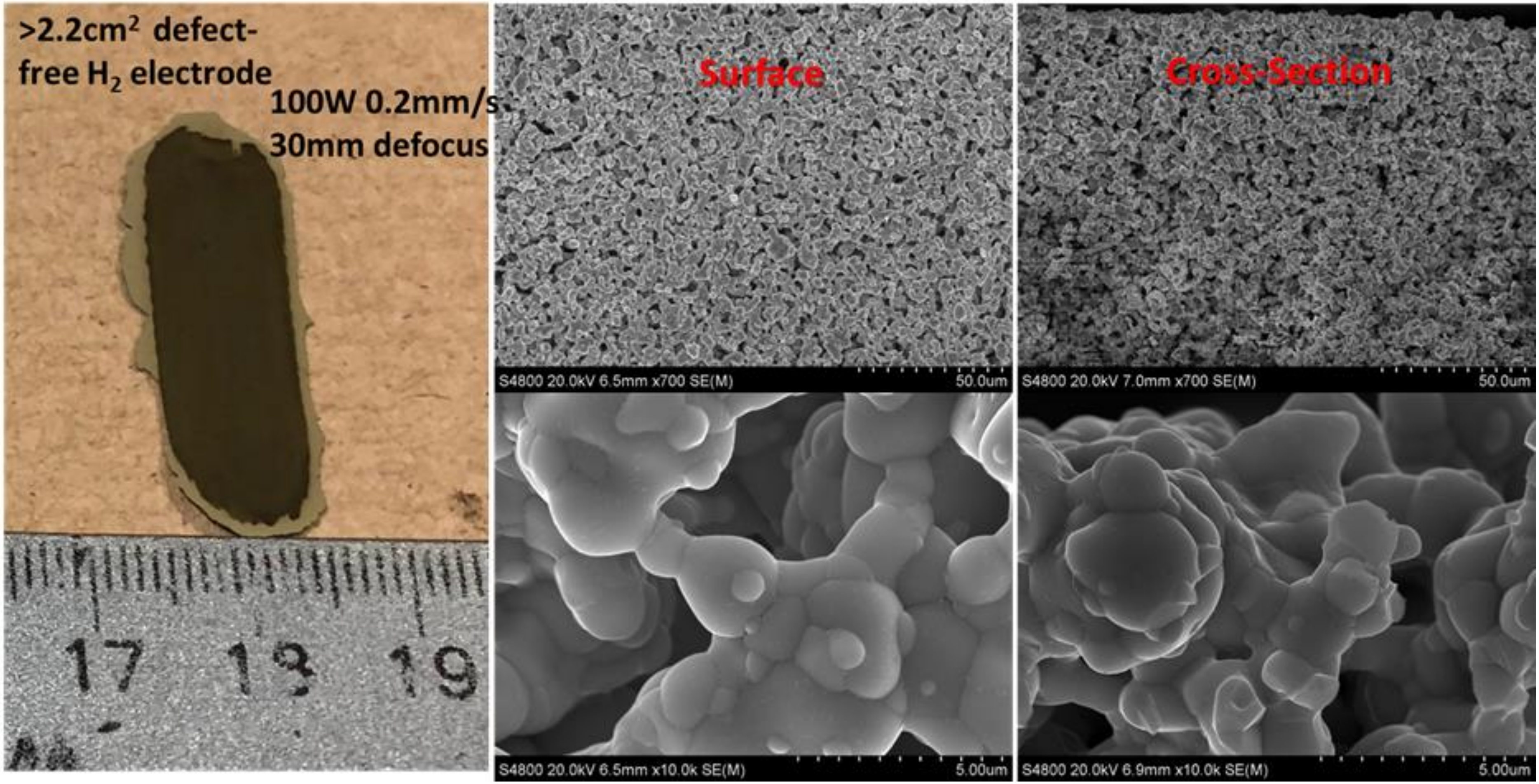
BCZYYb +1wt% NiO Electrolyte Thin Film



The line laser scan based on a cylindrical lens has been confirmed to be able to achieve fully densified BCZYYb+1wt% NiO electrolyte film on the reduced porous 40wt% BCZYYb + 60wt% NiO H_2 electrode substrates with an area **>2 cm²**.

MS4-RLRS of Component Thin Films

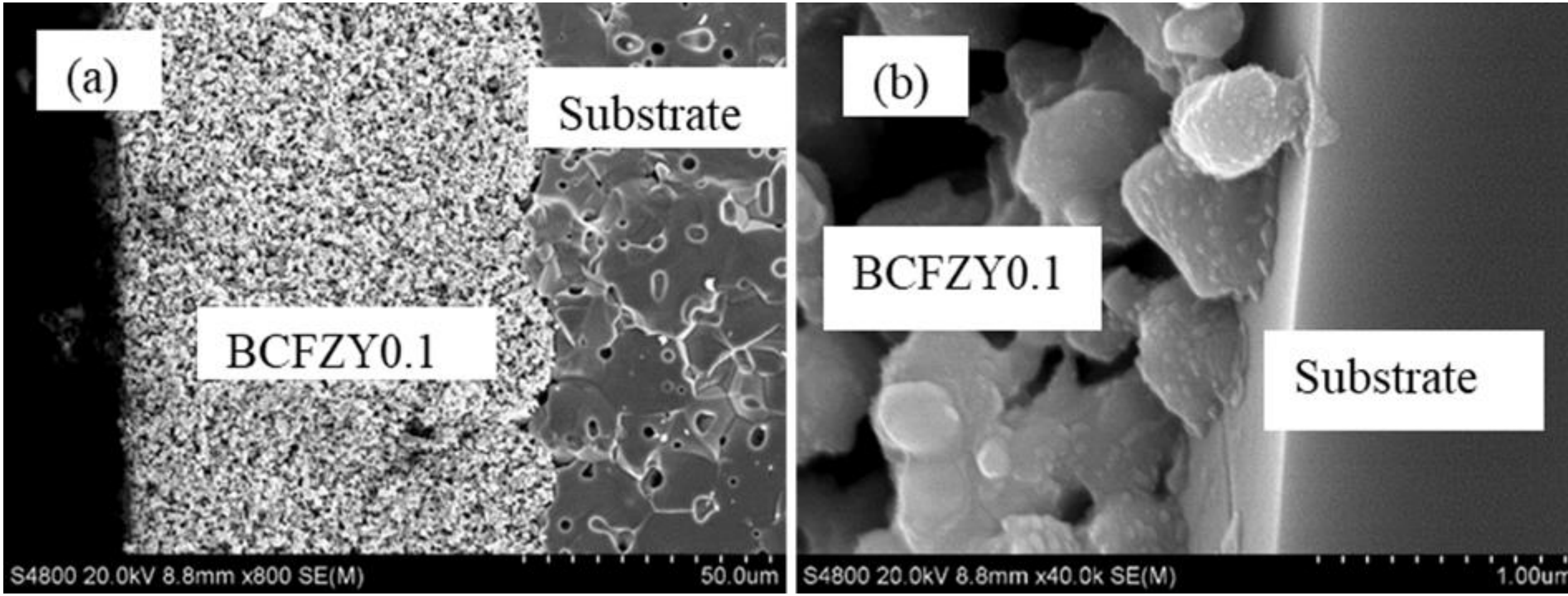
40wt% BCZYYb + 60wt% NiO H_2 Electrode



The defect-free porous 40wt% BCZYYb + 60wt% NiO H_2 electrode with an area **>2.2 cm^2** were obtained by laser sintering.

MS4-RLRS of Component Thin Films

BCFZY0.1 O_2 Electrode Films



Cross-sectional view of the BCFZY0.1 green powder film on dense BCZYYb substrate from the porous area: (a) low magnification image; (b) high magnification image at the interface between the layer and the substrate

The BCFZY0.1 O_2 electrode layers with **good porosity and small grain size** were obtained by laser processing paste from phase-pure BCFZY0.1 nanoparticle synthesized by a modified Pechini method.

Accomplishments and Progress:
Responses to Previous Year Reviewers' Comments

- Our project was not reviewed last year since this is a new project from November 6, 2018.

Collaboration & Coordination

- Clemson University is the sole recipient of this award. The collaboration & coordination mostly occur among the principal investigators.

PI. Jianhua "Joshua" Tong, Material Science and Engineering, Clemson University

Management and lead T3 PCES single cells by L3DP and T4 Five-cell PCES by L3DP and participate T1, T2, and T5.

Co-PI: Kyle S. Brinkman, Material Science and Engineering, Clemson University

Lead T-1 PCES materials development and participate T2 and T4

Co-PI: Fei Peng, Material Science and Engineering, Clemson University

Lead PCES Component Thin Films by L3DP and participate T3 and T4.

Co-PI: Hai Xiao, Electrical and Computer Engineering, Clemson University

Update and maintain L3DP equipment and Lead T-5 TEA and Market Transformation Plan and participate T3 and T4.

- Industrial advisory board is being established.
- Clemson is interested in partnering with lab and industrial collaborators.

Remaining Challenges and Barriers

As laser 3D printing of protonic ceramic electrolyzer stack, the overall challenge is to:

1) obtain thin green films by 3D printing based on the microextrusion technique
2) achieve large-area component films without any cracks by rapid laser consolidation technique
3) secure effective bonding between component layers.

Proposed Future Work

By Oct. 31, 2019

1	Discovery of new PCES materials (Discover compatible electrolyte, O_2/H_2 electrodes, and interconnect with low ASRs)
2	High materials performance in PCES single cells from selected materials fabricated by SSRS
3	3D printing of component large-area, crack-free green films
4	RLRS of component large-area crack-free thin films
5	Effective binding of PCES component films
6	Effective infiltration in the L3DP electrode nanoparticles showing OER and HER
7	Demonstrate high-performance PCES single cell fabrication by L3DP
8	The rough order of magnitude calculation to show the L3DP has potential to offer lower cost than conventional technologies
GNG	Demonstrate PCES single cells with area >5cm^2, current density >500mA/cm^2 at 1.3V and stable operation with a degradation rate <1% for >200h at 600°C by L3DP.

By Oct. 31, 2020

A PCES composed of >5 single cells with total area >100cm^2 will be manufactured by the L3DP technology. The current density >1A/cm^2 at 1.3 V and degradation rate <1% per 1000h at 600ºC will be successfully achieved.

Any proposed future work is subject to change based on funding levels

Technology Transfer Activities

- Our new laser 3D printing technology for manufacturing highly compacted multilayer ceramic energy devices such as fuel cell stacks, electrolyzer stacks, and ceramic membrane reactors are under development. The patent is being prepared and will be disclosed to Clemson University Research Foundation (CURF) for patent filing.

- The team is establishing industrial board and looking for industrial collaborators who are interested in either electrolyzer/fuel cell/hydrogen production or additive manufacturing of ceramic parts.

Summary Progress and Accomplishment

- The new electrolyte material of BCZYS was discovered with a total conductivity near to **$2x10^{-2}$ $\Omega^{-1}\cdot cm^{-1}$**.
- The new Ni-BCZYSm10 | BCZYSm10 | BCZY63-BCFZY0.1 single cell showed a peak power density of **313 mW/cm^2 at 600 ^oC** and current density **350 mA/cm^2 at 1.3 V and 600 ^oC**.
- The pastes for model component materials have been prepared for printing defect-free homogenous layers with **effective area >30cm^2**.
- The line laser scan based on a cylindrical lens has been confirmed to be able to achieve fully densified BCZYYb+1wt% NiO electrolyte film on the reduced porous 40wt% BCZYYb + 60wt% NiO H_2 electrode substrates with an **area >2 cm^2**.
- The defect-free porous 40wt% BCZYYb + 60wt% NiO H_2 electrode with an **area >2.2 cm^2** were obtained by laser sintering.

Technical Back-Up Slides

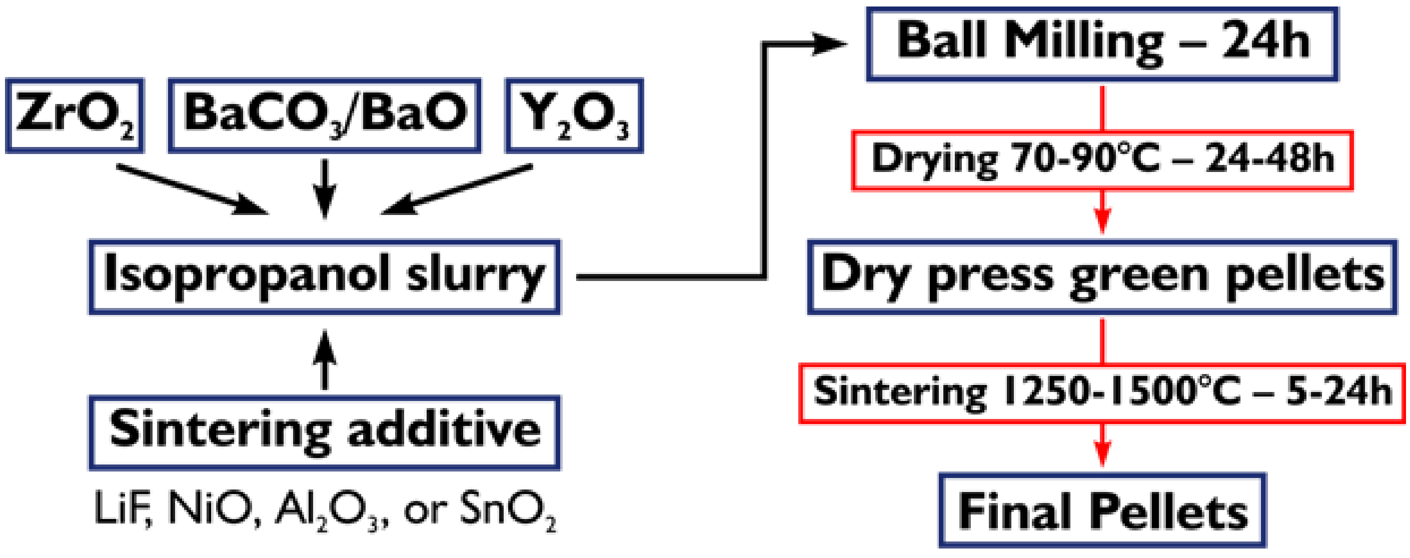
Abbreviations

3D, three dimensional
ASR, area specific resistance
BCF, a new triple conducting O_2 electrode with composition protection
BCFZY0.1, $BaCo_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1}O_{3-\delta}$
BCZY63, $BaCe_{0.6}Zr_{0.3}Y_{0.1}O_{3-\delta}$
BCZYS, a new electrolyte with composition protection
BCZYYb, $BaCe_{0.7}Zr_{0.1}Y_{0.1}Yb_{0.1}O_{3-\delta}$
BP, budget period
CURF, Clemson University Research Foundation
GNG, go / not go
HER, hydrogen evolution reaction
L3DP, laser 3D printing
LSCr, $La_{0.7}Sr_{0.3}CrO_3$
MS, milestone
OER, oxygen evolution reaction
PCES, protonic ceramic electrolyzer stack
RLRS, rapid laser reactive sintering
SSRS, solid state reactive sintering
T, task
TEA, technoeconomic analysis
TRL, technology readiness level

Solid State Reactive Sintering

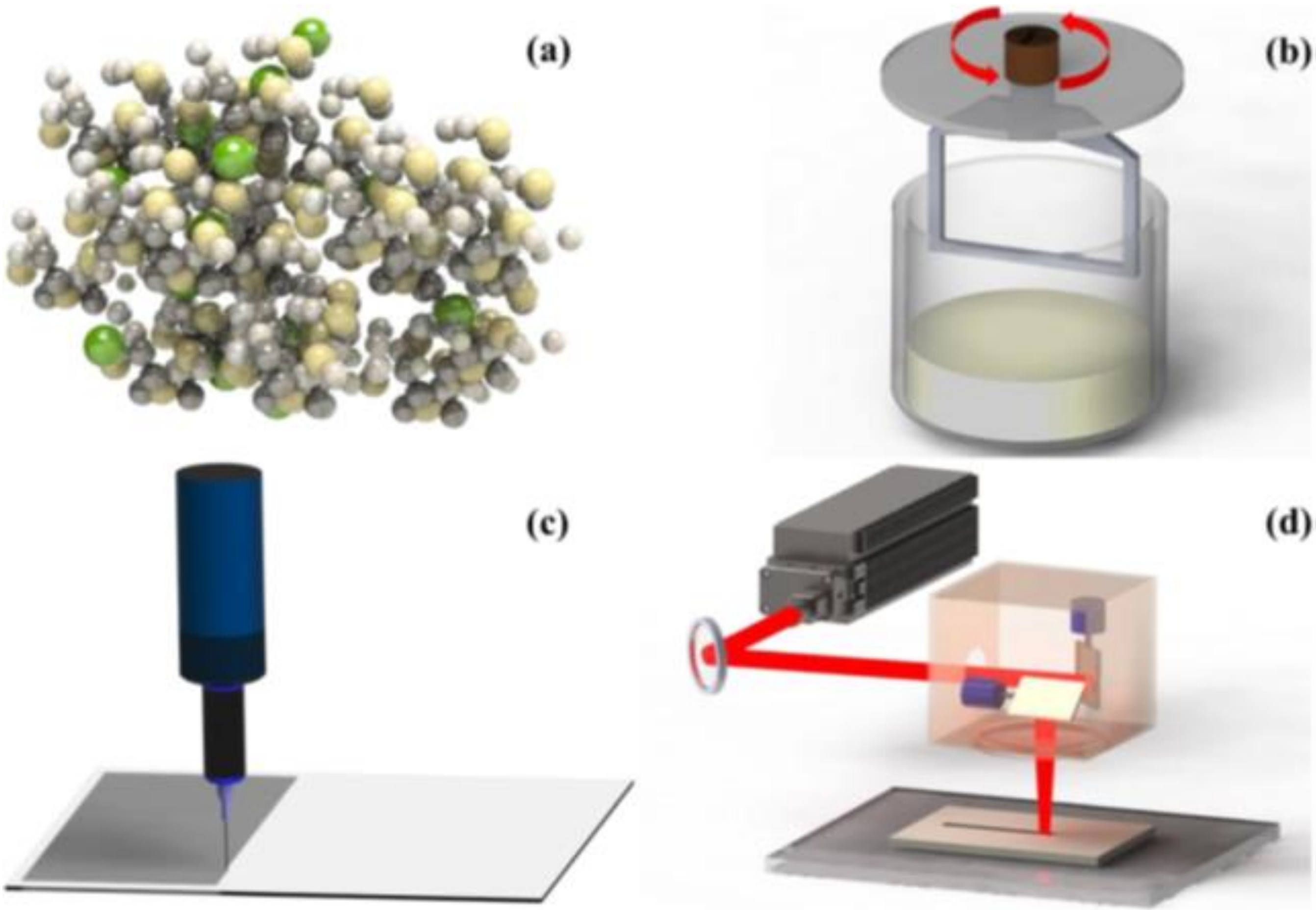
- **Cost-effective raw materials such as carbonates and oxides**
- **Small amount of sintering additives**
- **Single moderate-temperature sintering step**
- **Phase formation, ceramic densification, and grain growth are combined**

$BaZr_{0.8}Y_{0.2}O_3$ (BZY20) as an example



J. Tong et al., Solid State Ionics 2010, 181, 496-503

Rapid Laser Reactive Sintering



Schematic description of rapid laser reactive sintering (RLRS) process. (a) Mix precursor solids, (b) prepare precursor paste, (c) deposit precursor layer, and (d) perform RLRS

S. Mu and J. Tong et al., Solid State Ionics 320 (2018) 369–377