3D-Painted Solid Oxide Fuel Cells: A New Approach to Functional Multi-Ceramic Device Fabrication

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Let’s categorize “Additive Manufacturing” and “3D-Printing” (See ASTM F42)

**ENERGY-BASED**
- Laser Sintering (Powder Bed)
- Laser Melting (Powder Bed)
- Electron Beam Melting (Powder Bed)
- Stereolithography (Photo-cured Resin)

**DEPOSITION-BASED**
- Fused Deposition Modeling (Hololith Etralum)
- Inkjet Binding (Powder Bed)
- Direct Extrusion (Plast-O-Matic)
- Direct Ink Writing

**Instrument Driven**

**Material Driven**

Laser Metal Deposition

Originals Pioneered by 3D Systems
**“TRADITIONAL” METAL AM**

- **Energy-based**
  - Laser Sintering (Powder Bed)
  - Laser Melting (Powder Bed)
  - Laser Metal Deposition
  - Electron Beam Melting (Powder Bed)
  - Stereolithography (Monomer Bath) (not for metals)

Originally pioneered by 3D Systems

**Instrument Driven**

Primarily associated with metals

- Biomet

- High-power energy beam

- Powder-Bed

- Pratt and Whitney
DEPOSITION-BASED 3D-PRINTING

"Rapid Prototyping"

Primarily associated with thermoplastics
Where do ceramic materials fall?
The Shah Tissue Engineering and Additive Manufacturing Laboratory

Defining “3D-Printability” and creating and developing new, 3D-printable materials for any and all applications.
Science Translational Medicine, 2016.
(Cover)


Scientific Reports 2017.
Acta Astronautica. (In Review)
**Shah TEAM Lab 3D Printable Ink Platforms**

**Hydrogel/Cell-Based Inks**

*“PEGX Bioinks”*

- Aqueous-Based, Primarily Water Hydrophilic
- Multi-Mat. Compatible
- Can Encapsulate Live Cells (Bioprinting)

**Particle-Laden Inks**

*“3D-Painting”*

- Organic Solvent-Based
- Primarily Rigid Particles
- Multi-Mat. Compatible
- Can’t Encapsulate Live Cells

Well beyond biological and medical applications
3D-PAINTING: A COMPREHENSIVE, MATERIALS-CENTRIC APPROACH TO 3D-PRINTING & ADDITIVE MANUFACTURING

Not merely different colors... Completely different materials!

A selection of more than 300 distinct 3D-Inks developed by the Shah TEAM Lab
(...and can be mixed and modified ad infinitum)
Why “3D-Painting”: Let’s Take a Closer Look at Paint...

“3D-Paints” contain the same major components as household paints, but dry much quicker!
**3D-Painting**

- Room-temperature extrusion
- Deposition rates up to 150 mm/s*
- No powder beds or resin baths
- No Support materials required
- No curing or post-reactions to stabilize structures
- Objects can be handled immediately
- One to thousands of layers
- 100 µm to 2 mm** fiber diameter

* Maximum speed of our hardware, not material limited.
** Maximum diameter tested
3D-Paints are composed primarily of the functional particle/powder rather than of non-functional polymer.

Solidify via rapid evaporation of solvent upon extrusion.
A Selection of 70 vol.% Particle Inks

Inks do not settle-out over time

Long shelf-life (Printable for at least 24 months after synthesis)
No need to re-wet. Remain flexible for at least 4 years.
EFFICIENT AND SCALABLE SOLID OXIDE FUEL CELL FABRICATION VIA 3D-PAINTING

US Patent Application 15/212,534

“Efficient and Scalable Solid Oxide Fuel Cell Fabrication via Extrusion-based 3D-Printing of Liquid Inks” Manuscript in Preparation
Solid Oxide Fuel Cell Basics

\[ \text{H}_2 \ (g) + \frac{1}{2} \text{O}_2 \ (g) \rightarrow \text{H}_2\text{O} \ (g) + e^- \] at high temperature
Traditional Processing and Limitations

Fuel cells aren't economically viable for widespread adoption...yet
Revisiting Additive Manufacturing of Ceramics:

ENERGY-BASED

Laser Sintering
(Powder Bed)

Laser Melting
(Powder Bed)

Electron Beam Melting
(Powder Bed)

Originally Pioneered by 3D Systems

Instrument Driven

Stereolithography
(Resin-based)

DEPOSITION-BASED

Fused Deposition Modeling
(Heat-assisted Extrusion)

Inkjet Binding
(Powder-Based)

Direct Extrusion
(Presented)

Direct Ink Writing
Materials Driven

Laser Metal Deposition

Originally Pioneered by Stratasys

Materials (now part of 3D Systems)
Background: Attempts to Additively Manufacture SOFCs

Binder Jetting

- Little microstructural control
- Geometry Limitations

Inkjet Binding

- Only demonstrated electrolyte materials
- Size and Geometry Limitations

“Original and Proprietary” (Inkjet Binding)

- Multi-step firing procedure
- Size and Geometry Limitations


Require a versatile and scalable process to fabricate *monolithic* multi-ceramic fuel cell stacks without the need for labor-intensive assembly and non-functional, structural components...
Apply 3D-Painting to SOFC manufacturing!
No drying time required.

Objects can be handled immediately after being created.
Not a “push-button” technique, requires controlling >15 independent parameters
(i.e. applied pressure, linear speed, needle offset etc.)
Thermal Processing: 1250°C for 4 hrs.

3D-printed architecture maintained and desired microstructure achieved!
Electrochemical Measurements (800°C)

Current-Voltage Measurement

V$_{OC}$ = 0.283 V

> 1 V desired

Impedance Spectroscopy

R$_{Ohmic}$ $\sim$ 5 Ω

< 1 Ω desired

Relatively poor performance… for now.
Combine 3D-Printed and Tape-Cast Layers to Improve Electrochemical Performance

Good performance, but more cumbersome fabrication and assembly...not scalable!
Compatible Techniques: Dip-Coating

Provides additional versatility in fabrication!
Ink system can be utilized to create thin films as well as 3D-structures
Shrinkage manageable by tailoring ink composition.
Ink versatility provides many ‘knobs to turn’ for control.
Where are we going?

The Present

The FUTURE

Dip Coating

3D-Painting

Ink Casting

After Firing

LSM (cathode)

YSZ (electrolyte)

NIO + YSZ (anode)
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Xin Li, PhD
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