Solid Oxide Fuel Cell Manufacture by Computationally Driven Aerosol Jet Printing

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Abstract: *An innovative printing method, computationally driven aerosol jet deposition (AJP), has been successfully utilized for the manufacture of solid oxide fuel cells (SOFC). A model revealed that a functionally graded anode can simultaneously enhance SOFC performance and durability by decreasing the polarization resistance and thermal expansion coefficient mismatch. The layer-by-layer nature of aerosol jet deposition allowed functional grading in a single electrode processing step without adding manufacturing time. The process is scalable from lab to stack size.*

Keywords: solid oxide fuel cells; genetic algorithm; additive manufacturing; aerosol jet printing; functionally graded materials; thermal stresses; composites.

Introduction

Aerosol jet printing is an additive manufacturing method that enables deposition of functional inks comprised of colloidally dispersed metals, ceramics, or organics[1]. AJP permits structural control over the mesoscopic to macroscopic length scales. X-Y resolution is on the order of 10 microns and thickness resolution is on the order of the average particle size in the ink. AJP can also enable functional grading of materials (FGM) through simultaneous deposition of varying proportions of disparate materials. In the context of electrochemical energy storage devices, 3D printing has been used to fabricate electrodes and electrolytes not possible through conventional methods [2], [3]. AJP is appealing for manufacturing because of its ability to achieve high resolution electrode designs including tuned thickness, porosity, and composition, in a single processing step. An AJP M3D printer (Mesoscale Materials Deposition, Optomec Inc.) with a dual pneumatic atomizer is depicted in Figure 1. The independent atomizers allow material mixing during the printing process, as inks are blended in the deposition head.

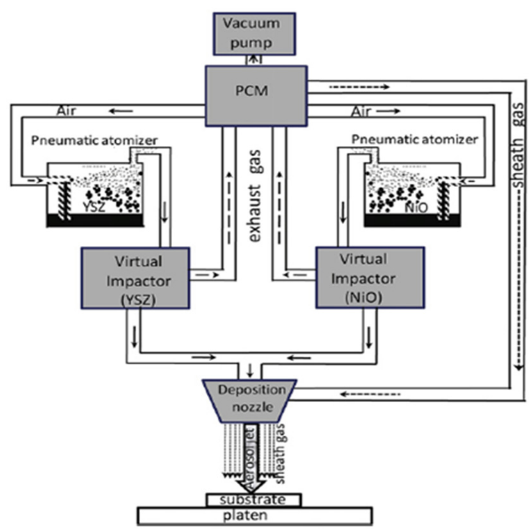


Figure 1. Schematic of Optomec AJP M3D Printer. Reproduced with permission from Elsevier [4].

Figure 2 depicts the process of printing full-size 100 cm^2 SOFC electrodes on an electrolyte substrate. The AJP method could be scaled to yet larger sizes by utilizing wider spray nozzles. Figure 3 displays a SEM image of an SOFC with printed anode, barrier layer, and cathode. Layer thickness resolution was ~ 1 micron.

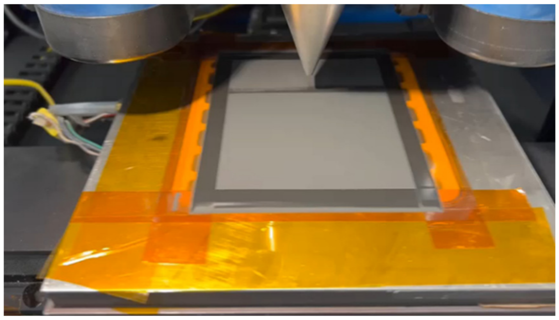


Figure 2. Depiction of 100 cm^2 cathode on electrolyte support.

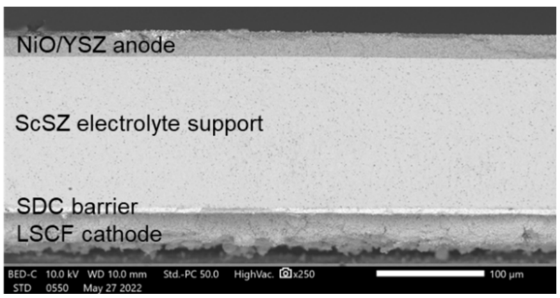


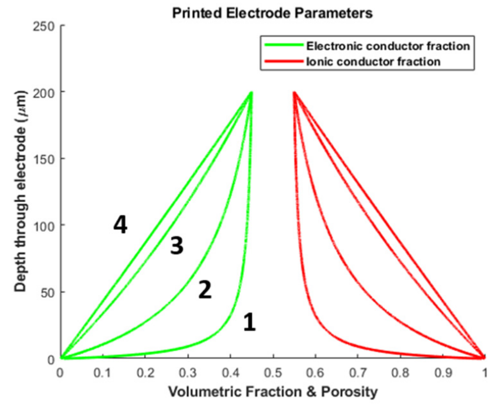
Figure 3. Cross-sectional SEM of AJ-Printed electrolyte-supported SOFC button cell

Design Methodology

Rational FGM SOFC Design via Computation

To guide the design of printed solid oxide cells, a computational model of a SOFC electrode has been created to predict the polarization resistance and thermal stresses present under operating conditions. The volumetric electrode is reduced to a one-dimensional boundary value problem (BVP) to numerically solve the local Butler-Volmer kinetics and percolating electronic and ionic conduction. The BVP is solved through finite difference collocation via the bvp5c algorithm within Matlab with a relative tolerance enforced at 1e-5. This algorithm uses the four stage Lobatto IIIa formula which is fifth order accurate within the boundary value range. To address the polarization resistance, maximal local value of overpotential, $\eta\,(V)$, is used as scoring criterion of resistance for a printed electrode design under consideration. The model also addresses the thermal stresses that arise due to the mismatch of the respective layers' thermal expansion coefficients which can lead to delamination in SOFCs [5]. Functionally graded materials (FGMs) represent a technique to eliminate discrete layers. The dependence of in-plane normal thermal stresses on the concavity of FGM profiles is shown in Figure 4. Local material properties are calculated through rules of mixtures introduced by Nemat-Alla [6] and are here applied to SOFC layer materials. The maximal absolute value of normal stress is a second scoring criterion for electrode designs.

(a)



(b)

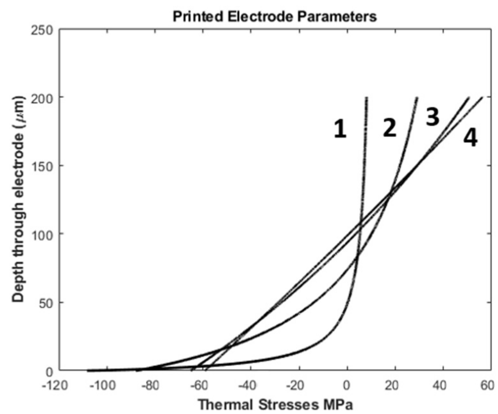


Figure 4. (a) SOFC Ni (electronic cond.) -YSZ (ionic cond.) electrode compositional grading profiles (0 µm= electrolyte) (b) Corresponding thermal stresses predicted

A genetic algorithm (GA), NSGA-II, is used to breed individual electrode designs. Microstructural parameters such as composite local phase fraction, mean grain size, grain size variance, porosity, and compositional profile concavity are considered as design variables. An example of a Pareto front produced by the optimization of a 30 µm thick Ni-YSZ anode is shown in Figure 5. Individual A, a noninferior solution and near-optimal compromise of objectives, had a mean YSZ grain size of 0.43 µm, Ni grain size of 0.41 µm, and porosity of 40%. The convergence of phase grain sizes under maximal performance is explained in [7]. The range of allowable grain sizes based on preprocessing available for commercial powders was set at 0.4-1.0 µm. It is predicted that the functionally graded Ni/YSZ anode with second-order profile would result in an overpotential reduction of the half-cell from 0.19 V to 0.14 V at a current density of 1.0 A/cm^2 and a thermal stress reduction from 76 MPa to 48 MPa as shown in Figure 6 compared to a homogeneous electrode. Both electrodes have a composition of Ni:YSZ 36:64 by percent solid volume at the current collector.

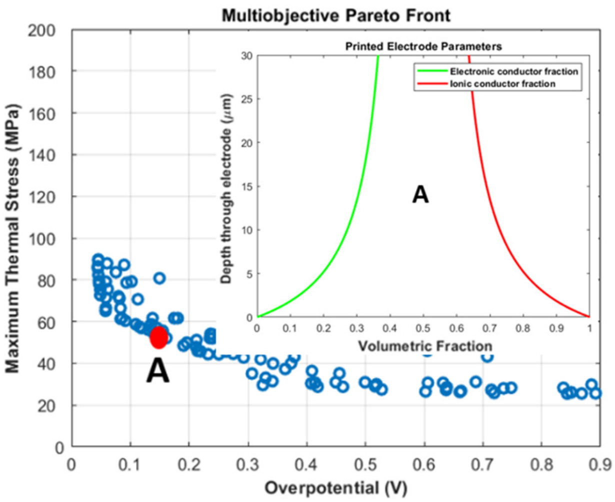
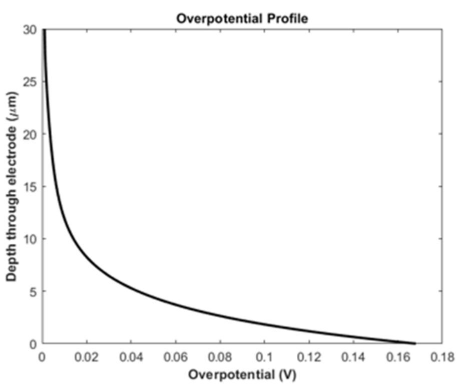


Figure 5. Pareto front of final generation of Ni-YSZ anode individuals with compositional grading profile inlay of individual "A" (Ni: green; YSZ: red)

(a)



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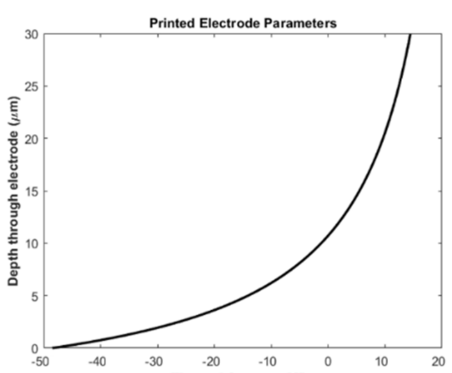

Figure 6. (a) Individual "A" Profile of Overpotential (b) Individual "A" Profile of Thermal Stresses

Functionally Graded Button Cell Printing

To achieve a functional graded anode structure, commercial NiO and YSZ powders (FC Materials) were colloidally dispersed to form jet printable inks. A suitably printable ink would have stably dispersed sub-micron particles, a room temperature viscosity < 40 mPas, and a low vapor pressure solvent [8]. Relative to other drop on demand techniques like inkjet printing, AJP can deposit inks with a solids loading range of 20 – 40 wt. %. The ink formulations for the printed SOFC anode included components present in traditional tape casting recipes, such as an ethyl cellulose binder for green strength, and plasticizers like benzyl butyl phthalate, polyalkylene glycol, and polyvinyl butyral. Ink stability was provided by a phosphate ester dispersant and enhanced by viscosity tuning with the polymeric binder and plasticizers. The ceramic loading was above 35 wt.%. Using this ink, a linearized grading profile was deposited via AJP as a first order approximation of the more complex quadratic profile "A". The linear profile has a lower predicted absolute maximum normal stress of 31 MPa compared to 48 MPa of the quadratic profile. The atomic weight percent of Ni and YSZ in the printed layer was assessed by EDX (Figure 7). Micron scale functional grading of the Ni/YSZ anode was achieved.

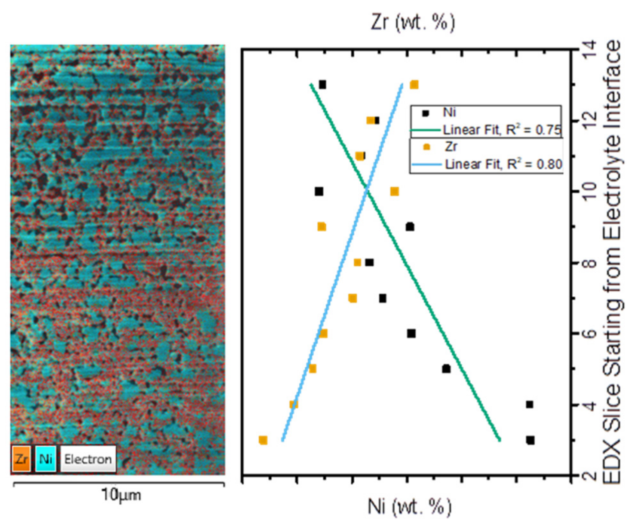

Figure 7. Overlay of EDX and SEM Image of Compositionally Graded Anode

Stack Scale SOFC Printing Verification

To demonstrate the scalability of the AJP process, full size 10 cm x 10 cm electrolyte supported SOFCs with homogeneous composition electrodes were printed. AJP was used to deposit a ~ 20 micron thick Ni/YSZ anode, ~20 micron thick LSCF cathode, and ~5 micron thick barrier layer of SDC. Even with compositionally homogeneous electrodes, precise control over layer thicknesses and the creation of seamless conformal interfaces may increase AJ printed cell performance over screen-printing or dip-coating methods.

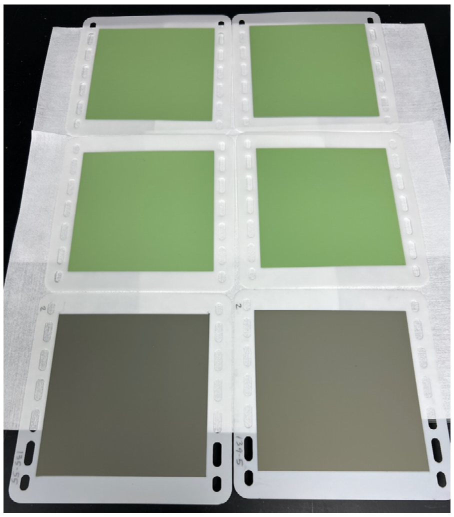

Figure 8. Finished 10 cm x 10 cm Printed SOFCs (upper two rows NiO-YSZ anode face up, lowest row LSCF cathode face up)

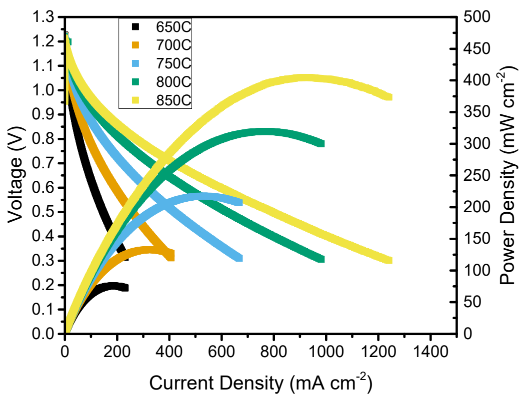

Figure 9. Electrochemical performance of AJ printed electrolyte-supported SOFC. Testing was performed in H_2(48 sccm)/air (150 sccm).

The electrochemical performance of AJ printed button cells using the same materials as the stack cells show a performance competitive with commercial cells despite commercial cells being tested at fuel/oxidant fluxes approximately an order of magnitude greater than the AJ printed cells [9].

Conclusions

Aerosol jet deposition provides fine geometric control of electrical and electrochemical components from the microscale to macroscale. Applied to SOFCs, both homogeneous and functionally graded cell layers benefit from this level of manufacturing precision. Enhancements in electrochemical performance are still being verified experimentally, while the ability to provide gradation at material interfaces to reduce stresses has been demonstrated.

Acknowledgements

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