Micro Solid Oxide Fuel Cell Fabrication via Inkjet Printing

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ABSTRACT

Energy conversion and storage devices are facing the challenge of manufacturing miniature dimensions and/or unconventional shapes. In this study, micro ceramic patterns are crafted via drop-on-demand (DOD) inkjet printing for potential application to micro solid oxide fuel cells (µSOFCs). This work focused on elucidating the influence of jet kinematics, jetting process parameters, and ink formulation on final deposition quality, resolution, and microstructure. A dilute solid-solvent colloidal ink suspension composed of a common SOFC cathode material [La\textsubscript{0.6}Sr\textsubscript{0.4}Fe\textsubscript{0.8}Co\textsubscript{0.2}O\textsubscript{3} (LSFC)] in α-terpineol with or without ethyl cellulose (EC) was used. The dilute nature of the ink necessitated multiple inkjet passes to achieve desired feature thickness and surface coverage. Jetting kinematics were tuned by adjusting temperature and velocity to obtain a range of Weber (0 < We <57) and Z values (0 < Z < 24). In addition, several process parameters (platen temperature, interlayer delay time, print height and substrate smoothness) were tuned to achieve a high degree of ink deposition accuracy on the x/y plane. Uniform circular micro dots (0-D dots) and straight-edged, smooth micro lines (1-D lines), respectively, are fabricated. A defect-free 0-D micro dot and 1-D line were fabricated that were devoid of splash, satellites, discontinuity, or bulging defects on the x and y axes. Further, unique ‘volcano’ features wherein the density gradation between the feature’s center and ridge were created, which could be beneficial for miniature SOFCs’ electrochemical properties.

Keywords: micro patterns, colloidal suspensions, LSFC cathode, “coffee ring effect”, ink kinematics

INTRODUCTION

Solid oxide fuel cells (SOFCs) are a very attractive power generation technology due to their high energy density, high efficiency, environmental friendliness, fuel-flexibility etc. Recent interest has focused on the miniaturization of SOFCs for mobile or portable applications. In particular, reduction in the length-scale of certain cell features have been found to significantly reduce the internal impedance which can potentially improve interfacial electrochemical kinetics leading to higher device performances [1, 2]. State-of-the-art micro SOFCs (µSOFCs), both in lateral and vertical dimensions, are currently fabricated using thin film deposition and micro-electro-mechanical-systems (MEMs) techniques. The latter involves a series patterning and etching processes that are rather complex, time-consuming, and cost prohibitive. Drop-on-demand (DOD) inkjet printing is a promising alternative approach for fabricating µSOFCs due to its low cost, noncontact fabrication, high throughput, and reproducibility. Recently, there has been increasing research in the use of inkjet printing for SOFCs [3, 4]. But investigations on the capability and limits of the fine-write processing have yet to be conducted for the benefits of µSOFC technology.

The objective of this work is to elucidate the limiting factors of inkjet processing for µSOFCs by exploring the influence of jet kinematics, inkjet process parameters and ink formulation on final micro feature quality, resolution and microstructure. In this study, high quality micro dots and micro lines, which are herein referred to as 0-D dots and 1-D lines, respectively, are fabricated. A defect-free 0-D feature refers to uniform, well-shaped circular dot with no imperfections in the vicinity of the dot from satellites or splash breakups. The 1-D lines are continuous, straight and narrow with parallel sides, which require regulation of the spacing between droplets to minimize line width as well as to avoid discontinuities and/or bulging at the line edges. Feature thickness (z-axis) of both 0-D dots and 1-D lines are produced by sequential deposition of that feature with high x,y accuracy.

EXPERIMENTAL

2.1 Inkjet Printer and Ink Formulation

All ceramic features studied in this manuscript were produced using a Fujifilm Dimatix DMP 2831 printer. This printer incorporates multiple DOD piezoelectrically-driven inkjets with adjustable print head temperature, platen temperature, firing voltage of individual jets, print-height, and drop spacing. The slew rate and frequency of the firing voltage were tailored to optimize the inherent acoustics of the inkjet to the physical properties of the ink formula. The amplitude of the firing voltage was adjusted to obtain the target droplet velocity.
The ink consisted of α-terpineol, LSFC, and ethyl cellulose (EC) wherein LSFC and EC contents were varied from 3.5–12 wt. % and EC from 0.0–0.1 wt. %, respectively. The solvent, α-terpineol, was chosen because its viscosity can be adjusted over a fairly broad range via temperature and still remain within the printer’s operating specifications. Average particle size of solids were ~ 100 nm to facilitate jetting. For multiple-pass droplet deposition study, the highest solids loading, i.e. 12 wt. %, was used to minimize the number of printing passes for pre-set feature thickness. To study the “coffee-ring effect”, 0.1 wt. % EC was added as a dispersant/stabilizer to the ink. Above this level of EC, the nozzles clogged immediately upon printing.

2.2 Kinematic Study

In this study, Weber number (We) and reciprocal Ohnesorge number (Z) were used to evaluate inkjet ink kinematics. They were calculated from experimentally determined surface tension, viscosity, and drop velocity. Surface tension was determined using a DuNouy Tensiometer. Viscosities were determined using an Anton Paar Rheolab QC rheometer. Video cameras integrated into the printer system were used to determine droplet velocity. The viscosity and surface tension were adjusted using fluid temperature, which differs from the previous work in which the viscosity and surface tension were controlled by solvent composition [5]. Droplet velocity was varied via manipulation of the jet voltage profile, which differs from previous studies that kept the voltage constant and altered velocity by pulse width.

2.3 Deposition Study

Deposition accuracy between ink passes were studied as a function of evaporation rates, interlayer delay time, print height and substrate smoothness. Evaporation rate was evaluated by varying the platen temperature from ambient conditions (~25 °C) to 60 °C. The interlayer delay time, which is the time it takes for the print head to complete one pass and start the next, was varied from 0 to 240 seconds. The print height, which is the distance of the inkjet nozzles above the platen, was varied from 0.25 mm to 1.5 mm. The substrate smoothness was varied using smooth and rough microscope glass slides.

0-D dots were fabricated by programming the printer to deposit ink droplets onto a single point using multiple print passes. To avoid any drop to drop interactions, the 0-D drops were printed 254 μm apart on the x and y axis. 1-D lines were fabricated by overlapping jetted drops on the x-axis, in rows of 1 mm or more in length. The thickness of the micro features was tuned by varying the number of inkjet print passes from 1 to 10.

2.4 Feature Property & Microstructure Characterization

Top view optical images of the printed 0-D and 1-D micro features were captured using a MEIJI MX optical microscope with the help of Motic Plus software. Detailed morphological information was further examined on a JEOL Scanning Electron Microscope (SEM). The thicknesses of the printed patterns were determined using an Alpha-Step® stylus profilometer.

RESULTS/DISCUSSION

3.1 Ink Jetting Kinematics

Fluid kinematic properties are frequently combined and notated in terms of dimensionless parameters to capture the relative contribution of forces on an object. The dimensionless We-number captures the relative importance of inertial forces to surface tension while the Z-number captures the relative importance of inertial forces to viscous forces (see equations in Reference 5). The ink rheological results indicated that viscosity decreases considerably while the surface tension changed insignificantly upon increasing ink cartridge temperature. Based on the obtained values in the temperature range of 40 °C to 60 °C, the corresponding Z number increased from 3 to 24. When droplet velocity was increased from 6 m/s to 9 m/s the We-number increased from 25 to 57.

The onset of satellite formation and the associated splash/satellite defects was found to correlate only to droplet velocity and consequently only the We-number in the range tested. Below a threshold We-number (i.e. We-number < 35), stable droplets without satellites or splash were observed throughout the entire Z range (3 ≤ Z ≤ 24) (see Figure 1). Above the threshold point, both satellites and

![Figure 1: Schematic of stable inkjet operation considering We-numbers and Z-numbers](image)
3.2 Inkjet Deposition and Print Accuracy

When multiple inkjet passes are required, printing accuracy from layer to layer must be sufficient to consistently land on the target spot dictated by the CAD design. Inkjet accuracy requires the jetted droplet to travel on a straight, consistent trajectory, to fully coalesce into a single spherical ball prior impacting with the substrate, and to have consistent radial flow patterns upon landing on the substrate. It was experimentally determined that low platen temperatures could lead to low feature resolution attributed to the low solvent evaporation rate. For instance the 0-D dot diameter printed on an ambient platen (~25 °C) is close at least twice the feature-size 0-D dots printed at 60 °C (see Figure 2a). Secondly, interlayer delay time may result in drying at the nozzle which reduces accuracy deposition (see Figure 2b). Print height that is overly high may prevent complete droplet coalescence prior to the impact with the substrate resulting in droplet disintegration in flight from frictional and/or gravitational effects (see Figure 2c). If the print height is too low the feature can have poor resolution due to the droplet not being fully coalesced. Finally, rough substrates may elicit irregular flow patterns at the printed perimeter due to the presence of tiny micro channels (see Figure 2d).

Optical images showing the effect of the combination of favorable print conditions, which is referred to as ‘optimal’, are seen in Figure 2e. It can be seen that the favorable conditions were vital to obtaining small, circular 0-D dots and 1-D lines with clean, straight, uniform, continuous edges. For the studied inkjet printer and ink systems, favorable printing/deposition accuracy was achieved at a 60 °C platen temperature, 0.7 to 1 mm platen print height, zero second interlayer delay time, and using the smooth glass substrate.

3.3 “Coffee Ring Effect”

The “coffee ring effect” has been theorized to result from an outward (radial) flow of solvent in the drying drop [6]. In the studied ink system which contained high content of EC, a very distinct coffee ring in the 0-D dot was observed. Increasing the printing passes resulted in the formation of a very dense ring of LSFC at the periphery of the feature with high z-axis growth and a more open structure at the center where z-axis height is less than half of the circumferential crest. After approximately 10 passes, volcano-like micro features were observed (see Figure 3). In contrast, the ink formula consisting of only LSFC and α-terpineol solvent, rendered a fairly minimal “coffee ring effect” for one to ten ink passes. This is probably associated with the high density of LSFC relative to the solvent (6.4 g/cm³ vs. 0.93 g/cm³ respectively) which resulted in the solid particles depositing out of the solvent vehicle almost instantaneously following deposition. Similar phenomena were reported for the case of yttria stabilized zirconia and silica [5,9] suspended in aqueous media. EC, acting as polymeric dispersant and binder, was found to facilitate LSFC staying suspended more effectively in α-terpineol based on sedimentation tests. EC is thought to impact solid stability in the solvent by reducing particle agglomeration, increasing LSFC/solvent affinity, and/or increasing the relative buoyancy of the solid to the

![Figure 2](image-url)  
Figure 2: Optical images of dots and lines using a range of suboptimal printer conditions vs. those printed at the completely favorable (or ‘optimal’) conditions.

![Figure 3](image-url)  
Figure 3: Top-view SEM images of EC containing 0-D dots fabricated with a) single and b) multiple inkjet passes and c) side-view SEM image showing the volcano-shaped dot obtained at 30-pass printing using the EC containing ink.
solvent. It is hypothesized that these functionalities facilitate the solid particles being readily pulled to the periphery by the solvent/EC, thus forming a distinct “coffee ring”.

While the coffee ring is generally undesirable for thin film fabrication, this unique feature may be advantageous to μSOFCs since the variation in porosity and density could be controlled to promote more favorable electrode/electrolyte microstructures. Specifically, gas conduction and electrokinetics may be increased within the more porous center region while the denser, outer region of the “coffee ring” feature could be designed to promote greater electrical and ionic conductivity (see Figure 4).

CONCLUSIONS

By controlling droplet/substrate interactions, judicious placement of the jetted droplets, and ink formulation, we have obtained micrometer patterns, e.g. micro 0-D dots and micro 1-D lines, with x/y dimensions < 100 μm and z axis dimensions < 1 μm, that are dense, porous, and/or networked, and furthermore, which are desired characteristics for the different components in μSOFCs. This research demonstrated that the inkjet process has the potential to engineer micro ceramic features with tunability of thickness and density to promote greater electrical and ionic conductivity as well as gas diffusion. The knowledge gained from this research may be useful to other micro all solid energy conversion and storage systems to decrease the barriers for low-cost and high-throughput manufacturing of power generation technologies.

References


