Advanced 3D Fabrication of Energy Conversion Device Structures
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Summary

The aim of this project was to begin the development of a new three-dimensional materials fabrication capability, Additive Layer Manufacturing (ALM).[1, 2] This initial 6 months of support allowed us to assess the feasibility of printing high-quality ceramic layers. In particular, a process was developed for printing layers of Yttria-Stabilized Zirconia (YSZ). This required the development of stable YSZ colloidal suspensions with appropriate particle size distribution and solids loading, along with surface tension and viscosity values that allow for inkjet printing. Furthermore, software was developed that provides greater control over the printing process than what is available in commercial document printer driver software. YSZ deposition rates were characterized. After some process development, YSZ layers printed onto NiO-YSZ supports and then fired at elevated temperatures were found to be of uniform thickness and high density. After application of a (La,Sr)(Fe,Co)O3 (LSFC) cathode, LSCF/YSZ/Ni-YSZ structures were tested at elevated temperature as a solid oxide fuel cell; the near-theoretical open-circuit potential observed is indicative of a dense pore-free electrolyte layer. Based on this initial success, next steps will be to develop inks/processes for depositing other cell active materials, leading to a capability to print entire electrochemical cells, and eventually to print novel 3D electrochemical cell structures. We are seeking further support, both here and in Denmark, for this continuing R&D effort.

Rationale

The advantage of ALM is the ability to fabricate complex 3D structures. The main rationale for this work was to develop a fabrication method allowing greater freedom to produce novel 3D-structured Solid Oxide Fuel Cells (SOFCs). Fuel cells (and similar devices operated as electrolyzers for energy storage) are especially interesting for this approach, because of their complex structure involving anode, electrolyte, cathode, interconnector, gas flow channels, and gas seals. However, the technique is also relevant to a range of energy conversion devices including batteries, thermoelectrics, and solar cells. High-temperature thermoelectrics, for example, typically consist of two different oxide semiconductors along with interconnectors and open gaps – a structure consisting of many such devices can be fabricated in the green state by ALM, and then converted to a finished device array by high-temperature firing. Similarly, Graetzel-type solar cells consist of an oxide backbone (e.g., TiO2) and current collectors that can be fabricated by ALM and fired to produce the desired oxide structure. Flow batteries have similar requirements, although they utilize liquids instead of gases.

Description

The initial work was done using two inexpensive Epson Artisan inkjet printers (Figure 1). While these printers do not provide all the features and control of a technical printer, the cost is > 100x less ($150 versus ≥ $50,000). There is one potential advantage of the Epson printer – the liquid
volume per print droplet is more than in the advanced printers, which is useful for reducing the number of prints required to produce thick layers.

One of the requirements of using the Epson printer is that the ink must match the characteristics of the conventional inks. Thus the Epson magenta ink was characterized for its viscosity and surface tension. Inks were formulated using environmentally friendly water-ethanol mixtures that matched the desired characteristics. Also included were the YSZ powder and appropriate dispersants. Another ink requirement is that the YSZ particle sizes be relatively small; this so that the particles do not clog the orifices of the inkjet device. Various means including milling and filtering were use to eliminate larger particles, and size distributions were measured. Problems with orifice clogging were still observed, so further development with smaller YSZ particle sizes is warranted.

Initial characterization of the YSZ layers was carried out. After this, YSZ layers were printed onto NiO-YSZ supports and then fired at 1400°C (a typical condition used for firing YSZ). The YSZ layers appeared uniform and dense over their entire surface. SEM observations (Figure 2) proved that the YSZ layer was indeed dense and uniform; even though the thickness was only 3 μm, it was impermeable and gas-tight. A layer of (La, Sr)(Fe, Co)O3 (LSFC) was then deposited to serve as a cathode for the solid oxide fuel cell, with the YSZ layer being the electrolyte and the NiO-YSZ being the anode (after reduction of the NiO to Ni at the onset of cell testing).

The LSFC/YSZ/Ni-YSZ structure was tested under nominal solid oxide fuel cell operating conditions: elevated temperatures ranging from 650 - 800°C with air at the cathode and humidified hydrogen at the anode. Figure 3 shows the current-voltage characteristics. The open-circuit potential was ~ 50 mV below the theoretical Nernst potential for these conditions. However, this is usually observed in this test setup due to imperfect gas seals, and hence this result is consistent with the observation that the inkjet printed YSZ layer was dense and pore-free. The current densities measured here were small relative to the values normally measured for good SOFCs under these conditions. This is readily explained by the non-ideal electrodes
used in these tests. Note that impedance spectroscopy measurements showed that the electrolyte resistance was low and as expected for a 3 µm thick YSZ layer.

**Outcomes and Future Work**

Note that an electrode ink was also prepared during this work. However, printing has not yet been attempted. This will be done in the near future.

Søren Jensen’s six-month visit, enabled by the ISEN grant, accomplished its goals of demonstrating feasibility of device layer fabrication by inkjet printing, and establishing a baseline ALM capability. There is clearly enough data to support submission of proposals aimed at using ALM for making fuel cells and other energy devices. Our plan is to submit a proposal for joint research between Northwestern and Denmark. Work will continue both here and at Risø, albeit at a lower level, until support is obtained.

Finally, note that two Materials Science Masters degree students, Wei-Hang Chen and Yuanchi Chiang, worked on this project and received credit for a 499 research course as part of their MS degree requirements.

**Publications:**


**Proposals:** none yet