July – September 2023 report

Summary of accomplishments this period

In this period, we followed our work on 3D printing anode support for solid oxide fuel cells, SOFC (or cathode for solid oxide electrolyzers, SOEC) based on our designed optimization outlined in the previous report. We worked on optimizing the printing parameters, obtaining binder burn out and sintering profiles to obtain printed parts with desired geometry and properties.

Activity

To gain a deeper understanding of the printability of the 3YSZ photocurable slurry, we conducted rheology experiments to assess its viscosity at varying shear rates. The rheological properties of a ceramic slurry are crucial, often determining the characteristics of the final ceramic component. In stereolithography, it is required to use suspensions showing shear-thinning behavior and high solid loading to ensure the successful creation of flawless green bodies.

For effective digital light processing (DLP) printing, it is widely acknowledged that the resin's viscosity should remain below 20 Pa.s within the shear rate range of 10 (1/s) to 100 (1/s) [1]. Additionally, according to the research by M.L. Griffith and J.W. Halloran, the suspension viscosity should not surpass 3 Pa.s at a shear rate of 30 (1/s) to guarantee proper flow during the recoating process [2], [3].

As shown in Figure 1, elevating the temperature resulted in a significant decrease in the viscosity of the 3YSZ slurry, dropping below 2 (1/s). This indicates that at a temperature of 45°C, the printability substantially improves, leading to nearly defect-free fabrication of the green body. Consequently, optimizing the temperature during the printing process emerges as a critical factor in ensuring the quality of the ceramic parts produced.

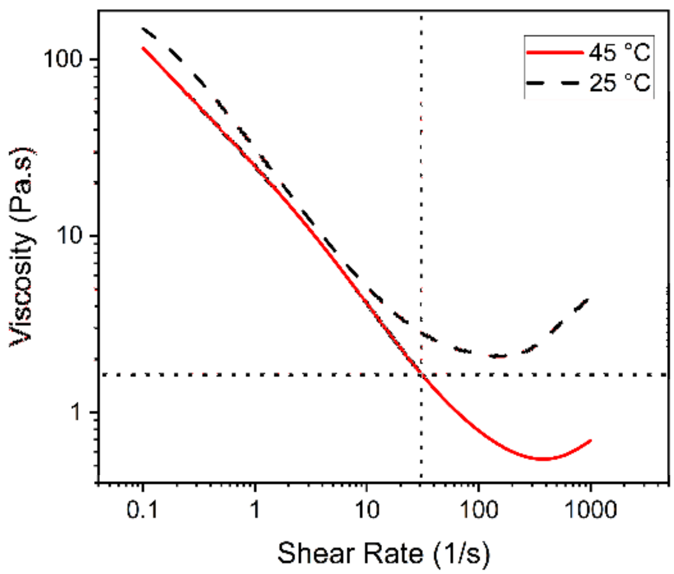

Figure 1. Rheological property of the 3YSZ photocurable slurry at different temperatures.

To optimize the debinding and sintering process, the DSC/TG experiment was conducted.

The TG-DSC curves presented in Figure 2 demonstrate the behavior of the 3YSZ printed using DLP method. It is evident from the figure that a significant portion of volatile organic matter was evaporated and decomposed within the temperature range of 220-520 °C from the green body. This process is followed by an exothermic oxidation reaction, which peaks at temperatures of 232 °C, 383 °C, and 430 °C. Consequently, only the ceramic material remains within the printed part after this debinding stage. Based on the TG-DSC curves the binder burn out and sintering was designed.

The debinding process involved a heating rate of 0.5 °C/min, with several hours of holding time at 220 °C, 430 °C, and 520 °C. Additionally, substantial weight losses was observed within the temperature range of 200-380 °C. As a result, the temperature ramp was kept at 0.25 °C/min to prevent introducing new defects inside the printed part.

Following the debinding process, the 3D printed 3YSZ was sintered up to desired final temperature (for example1400 °C) with a heating rate of 2.5 °C/min, followed by a 3-hour plateau. Finally, the bodies gradually cooled down from 1400 °C to room temperature over a period of approximately 9 hours.

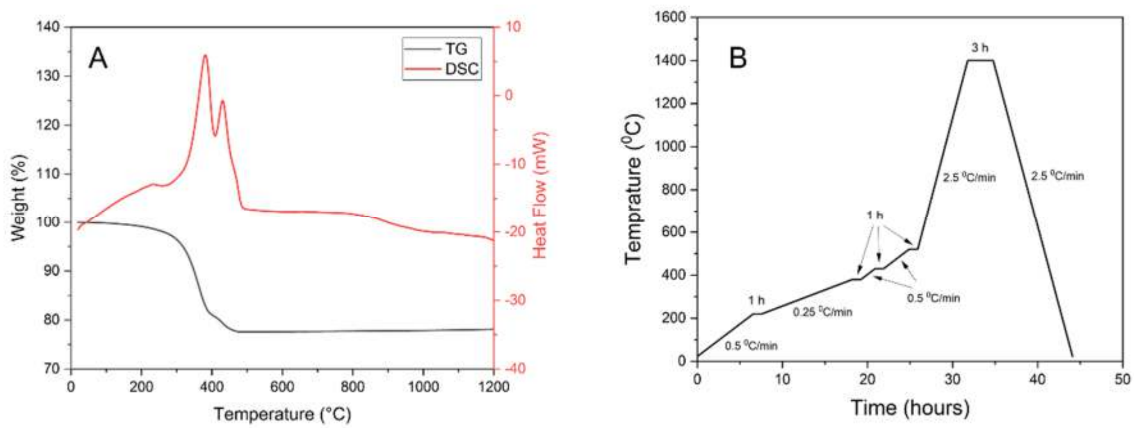

Figure 2 (A) The TG/DS curves (B) Designed debinding and sintering profile for 3D printed 3YSZ.

Following the detailed optimization of both the print temperature and the binder burnout-sintering profile, we proceeded to print cube-shaped structures to assess the shrinkage and density of the 3YSZ material. In Figure 3, it is evident that the sample experienced noticeable shrinkage after undergoing the sintering process at 1450 °C. Upon closer examination through microscopic analysis, it was observed that the printed layers underwent significant densification post-sintering. Importantly, this densification occurred without the emergence of any cracks or defects in the final printed product. These results not only affirm the effectiveness of the optimized parameters but also highlight the robustness of the printing process, showcasing its ability to yield compact, almost defect-free ceramic components.

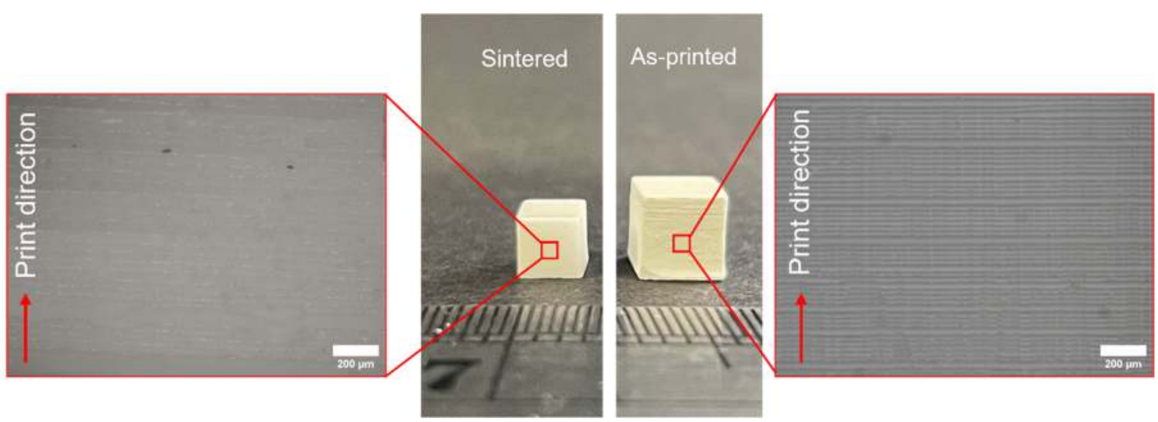

Figure 3. Microscopic image of as-printed and as-sintered.

Currently we are working on finding porosity in different temperature of sintering, as well as relative density to target the desire porosity for application of SOFCs and SOECs electrodes.

References

[1] Z. Chen, J. Li, C. Liu, Y. Liu, J. Zhu, and C. Lao, “Preparation of high solid loading and low viscosity ceramic slurries for photopolymerization-based 3D printing,” *Ceram. Int.*, vol. 45, no. 9, pp. 11549–11557, 2019.

[2] D. A. Komissarenko *et al.*, “DLP 3D printing of scandia-stabilized zirconia ceramics,” *J. Eur. Ceram. Soc.*, vol. 41, no. 1, pp. 684–690, 2021.

[3] M. L. Griffith and J. W. Halloran, “Freeform fabrication of ceramics via stereolithography,” *J. Am. Ceram. Soc.*, vol. 79, no. 10, pp. 2601–2608, 1996.