7th Quarterly Report
July-September 2023
AESF Research Project #R-123

Electrochemical Manufacturing for Energy Applications

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Editor's Note: *The NASF-AESF Foundation Research Board selected a project on electrodeposition toward developing low-cost and scalable manufacturing processes for hydrogen fuel cells and electrolysis cells for clean transportation and distributed power applications. This report covers the 7th quarter of work, from July to September 2023. A printable PDF version of this report is available by clicking* ***HERE****.*

1. Introduction

Hydrogen has been identified by the US government as a key energy option to enable full decarbonization of the energy system.[1] The US government has recently initiated a significant investment in the Hydrogen Economy, which is detailed in the recent "*Road Map to a US Hydrogen Economy: reducing emissions and driving growth across the nation*" report. In June 2023, the first ever "*US National Clean Hydrogen Strategy and Roadmap*" was published.[2] On Nov. 15, 2021, President Biden signed the Bipartisan Infrastructure Law (BIL). The BIL authorizes appropriations of $9.5B for clean hydrogen programs for the five-year period 2022-2026, including $1B for the Clean Hydrogen Electrolysis Program. In alignment with the BIL and the mission of Hydrogen Energy "*Earthshot*" to reach the goal of $1 per 1 kg in 1 decade ("1 1 1"), the US is projected to invest in priority areas that will advance domestic manufacturing and recycling of clean hydrogen technologies.

Solid oxide electrolyzer cells (SOECs) are energy storage units that produce storable hydrogen from electricity (more recently increasingly from renewable sources) and water (electrolysis of water).[3] The majority (~95%) of the world's hydrogen is produced by the steam methane reforming (SMR) process that releases the greenhouse gas carbon dioxide.[4] Electrolytic hydrogen (with no pollution) is more expensive compared to hydrogen produced using the SMR process. Investments in manufacturing and process development and increasing production scale and industrialization will reduce the cost of electrolytic hydrogen. Based on the recent DOE report, with the projected growth of the hydrogen market, the US electrolyzer capacity will have to increase by 20% compound annual growth from 2021 to 2050, with an annual manufacturing requirement of over 100 GW/yr. Given the complex structure and stringent physical

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and functional requirements of SOECs, additive manufacturing (AM) has been proposed as one potential technological path to enable low-cost production of durable devices to achieve economies of scale, in conjunction with the ongoing effort on traditional manufacturing fronts.[5] Recently (2022), the PI published an article on challenges and opportunities in AM of SOCs,[5] in which a comprehensive review of the state-of-the-art in this field is presented.

In this work, we aim to contribute to such effect of national interest to enable the hydrogen economy through development of manufacturing processes for production of low cost, durable and high efficiency solid oxide fuel cells (SOFCs) and SOECs.

2. Summary of Accomplishments (July-September 2023 Quarter)

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.

3. 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).[6] 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.[7,8]

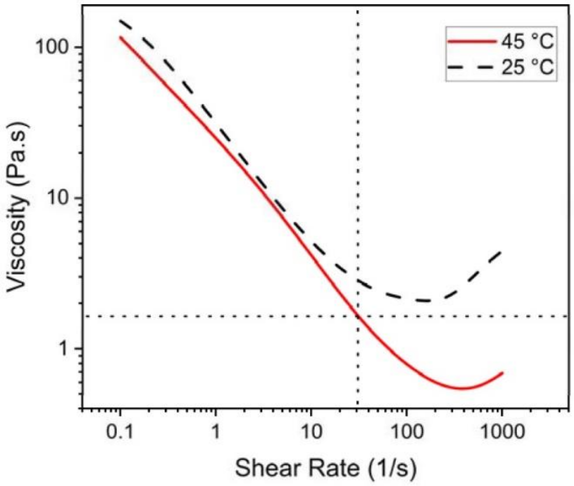

Figure 1 - Rheological property of the 3YSZ photo-curable slurry at different temperatures. To optimize the debinding and sintering process, the DSC/TG experiment was conducted.

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.

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 loss 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 the desired final temperature (*e.g.*, 1400°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.

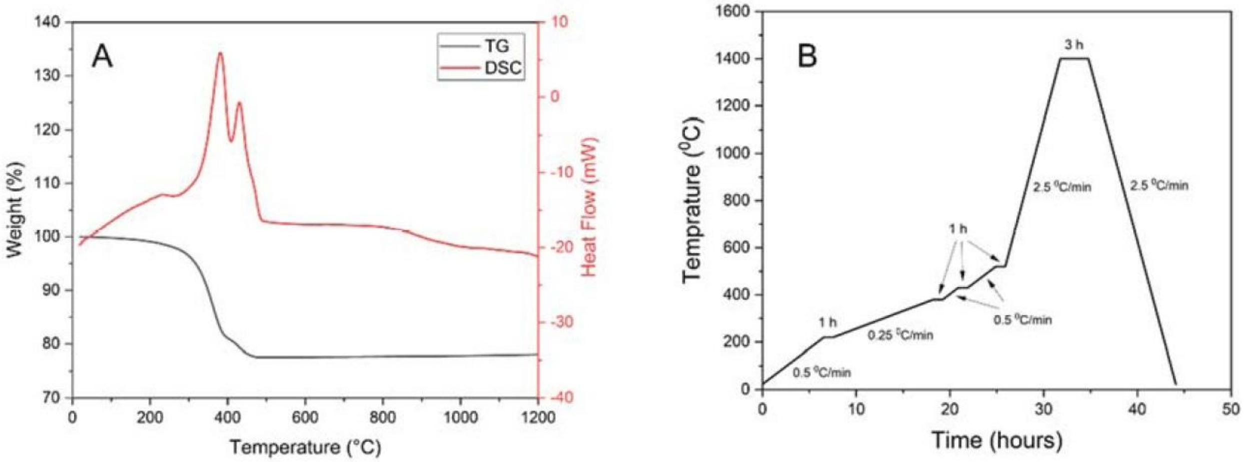

Figure 2 - (A) The TG/DS curves (B) Designed debinding and sintering profile for 3D printed 3YSZ.

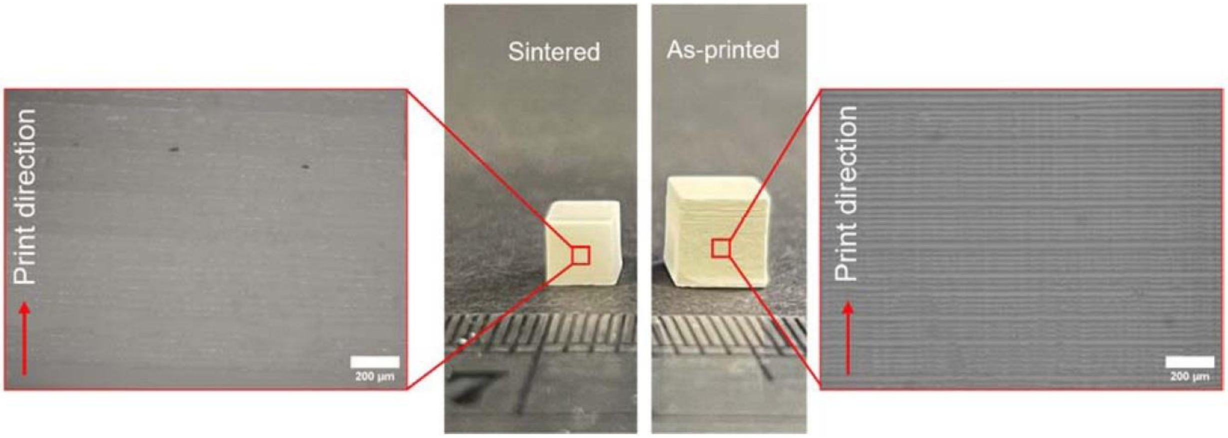

Figure 3 - Microscopic image of the as-printed and as-sintered conditions.

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. On 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.

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

4. References

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5. Past project reports

1. Quarter 1 (January-March 2022): Summary: *NASF Report* in *Products Finishing*; *NASF Surface Technology White Papers*, **86** (10), 17 (July 2022); Full paper: http://short.pfonline.com/NASF22Jul1 .
2. Quarter 2 (April-June 2022): Summary: *NASF Report* in *Products Finishing*; *NASF Surface Technology White Papers*, **87** (1), 17 (October 2022); Full paper: http://short.pfonline.com/NASF22Oct2 .
3. Quarter 3 (July-September 2022) **Part I**: Summary: *NASF Report* in *Products Finishing*; *NASF Surface Technology White Papers*, **87** (3), 17 (December 2022); Full paper: http://short.pfonline.com/NASF22Dec2.
4. Quarter 3 (July-September 2022) **Part II**: Summary: *NASF Report* in *Products Finishing*; *NASF Surface Technology White Papers*, **87** (4), 17 (January 2023); Full paper: http://short.pfonline.com/NASF23Jan1.
5. Quarters 4-5 (October 2022-March 2023) Summary: *NASF Report* in *Products Finishing*; *NASF Surface Technology White Papers*, **88** (1), 17 (October 2023); Full paper: http://short.pfonline.com/NASF23Oct1.
6. Quarter 6 (April-June 2023) Summary: *NASF Report* in *Products Finishing*; *NASF Surface Technology White Papers*, **88** (1), 17 (October 2023); Full paper: http://short.pfonline.com/NASF23Oct2.

6. About the Principal Investigator for AESF Research Project #R-123

Majid Minary Jolandan is Associate Professor of Mechanical Engineering at The University of Texas at Dallas, in Richardson, Texas, in the Erik Jonsson School of Engineering. His education includes B.S. Sharif University of Technology, Iran (1999-2003), M.S. University of Virginia (2003-2005), Ph.D. University of Illinois at Urbana-Champaign (2006-2010) as well as Postdoctoral fellow, Northwestern University (2010-2012). From 2012-2021, he held various academic positions at The University of Texas at Dallas (UTD) and joined the Faculty at Arizona State University in August 2021. In September 2022, he returned to UTD as Associate Professor of Mechanical Engineering. His research interests include additive manufacturing, advanced manufacturing and materials processing.

Dr. Minary is an Associate Editor for the *Journal of the American Ceramic Society*, an Editorial Board member of *Ceramics* journal and the current chair of the materials processing technical committee of ASME.

Early in his career, he received the Young Investigator Research Program grant from the Air Force Office of Scientific Research to design high-performance materials inspired by bone that can reinforce itself under high stress. This critical research can be used for aircraft and other defense applications, but also elucidates the understanding of bone diseases like osteoporosis. In 2016, he earned the Junior Faculty Research Award as an Assistant Professor at the University of Texas-Dallas – Erik Jonsson School of Engineering.