8th Quarterly Report
October-December 2023
AESF Research Project #R-123

Electrochemical Manufacturing for Energy Applications

by
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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 8th quarter of work, from October to December 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 (October-December 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 reports. We worked on the effect of sintering temperature on the amount of porosity and grain size in 3D printed yttria-stabilized zirconia (YSZ).

3. Activity

To understand the effects of sintering temperature on shrinkage, porosity and grain size, cubes with dimensions of 4 × 4 × 4 mm were printed. The printed cubes were then sintered at different temperature profiles ranging from 1100°C to 1450°C (Figure 1).

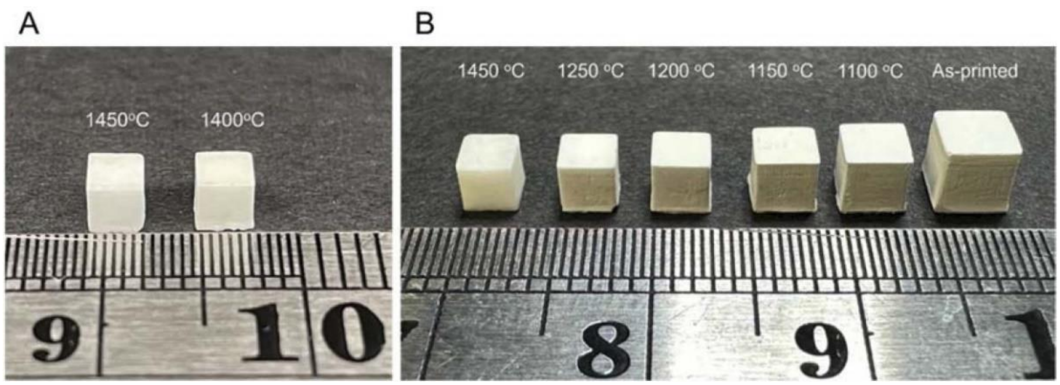

Figure 1 - Green and sintered body of 3D printed 3YSZ.

The SEM images of the sintered body of the 3D printed 3YSZ cubes were acquired at different sintering temperatures, as shown in Figure 2. Sintering was observed to be generally associated with shrinkage of the cubes because of the densification of the grain structure, which considerably reduced the porosity of the material. In contrast, the grain size gradually increased in the 3D printed 3YSZ sintered body as the sintering temperature increased.

Figure 2(G) demonstrates shrinkage of the cubes in x-y plane and z (print) direction. As the sintering temperature increased, a minimum of ~12 and 14% and a maximum of ~14 and 26% shrinkage for in-plane and print direction was observed at 1100°C and 1450°C, respectively (Table 1). In a similar study, for 3D printed 3YSZ material, the horizontal and vertical shrinkages were reported to be ~24% and 30% at the sintering temperature of 1450°C, respectively.[1]

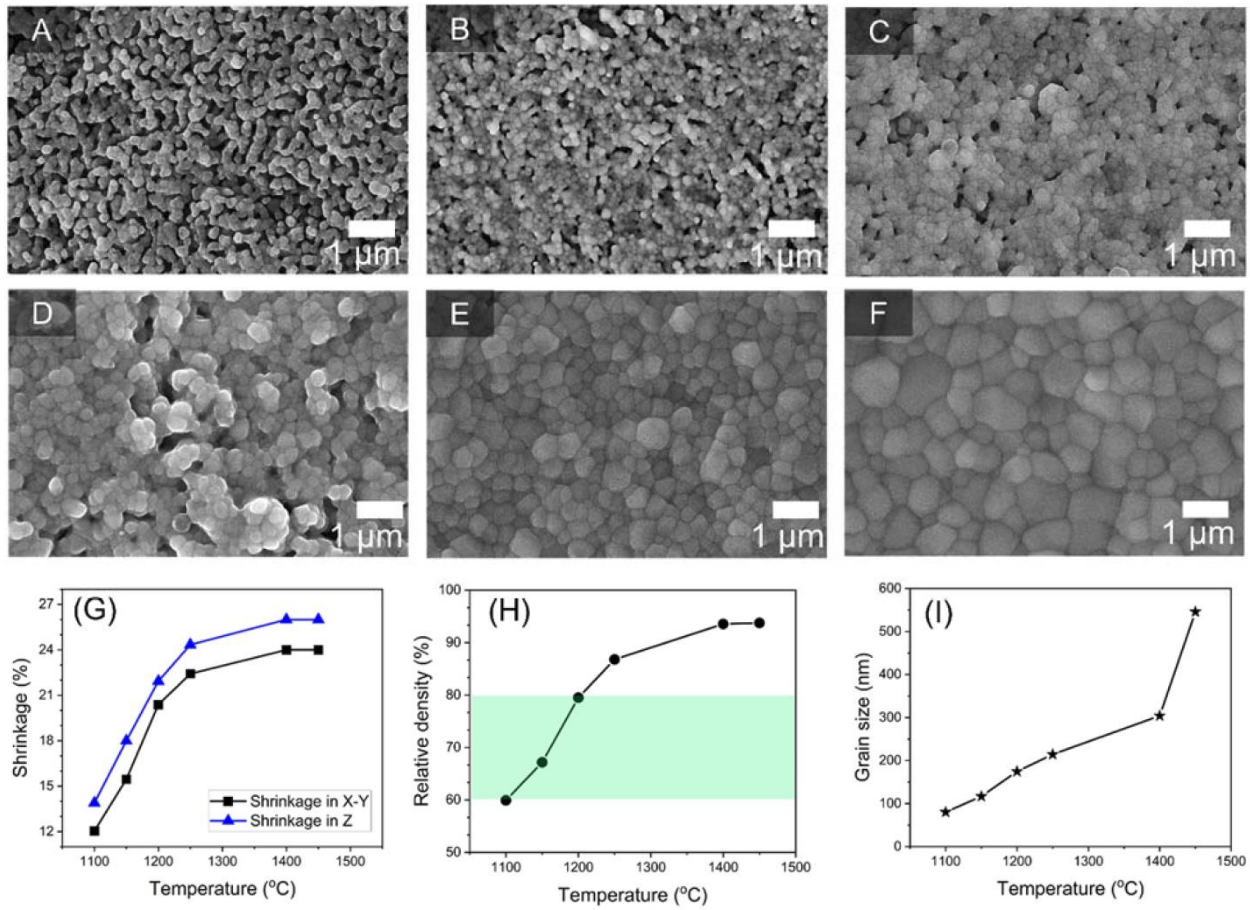

Figure 2 - SEM images of 3D printed 3YSZ sintered body at different temperatures: (A) 1100°C, (B) 1150°C, (C) 1200°C, (D) 1250°C, (E) 1400°C and (F) 1450°C. Figures (G), (H), and (I) show shrinkage, relative density and grain size at different sintering temperatures, respectively.

Table 1 - Shrinkage, porosity/density and grain size vs. sintering temperature.

Temperature (°C)	Shrinkage in X-Y (%)	Shrinkage in Z (%)	Porosity (%)	Density (g/cm^3)	Relative Density (%)	Grain size (nm)
1100	12	14	40	3.6	60	80
1150	15	18	33	4	67	115
1200	20	22	20	4.8	80	175
1250	22	24	13	5.2	86	215
1400	24	26	6	5.6	94	305
1450	24	26	6	5.6	94	550

The relative density and grain size of the sintered body of the 3D printed 3YSZ cubes were analyzed according to the sintering temperature, as shown in Figures 2(H and I). The relative density was measured by the Archimedes method, ranging from 60% to 94% for sintering temperatures of 1100°C and 1450°C, respectively (Table 1). Using the line intercepting method according to the ASTM standard E112-13,[2] the average grain size was estimated to be ~80 nm for a sintering temperature of 1100°C and ~550 nm for a sintering temperature of 1450°C.

According to sintering theory,[3] a three-step sintering mechanism was identified. The first stage occurred around 1100°C and was characterized by particle rearrangement, including the sliding and rotation of grains. This stage contributed to the formation of grain boundaries and an increase in the grain size. Moving to the second stage, which occurred at approximately 1250°C, cooperative particle rearrangement and atomic diffusion became the governing mechanisms. This stage was significant, as it began reduction of the pores within the sintered body. It was during this phase that the densification process continued. As the sintering temperature was further elevated to 1450°C, strong grain growth was observed. This resulted in the sintered body becoming even more compact, and it reached its maximum values of relative density and grain size.[1]

The potential uses of porous YSZ include serving as electrodes in SOFCs and SOECs, among other applications. In both applications, the amount of porosity of the electrodes is crucial for ensuring reliable operations. This porosity allows for sufficient gas diffusion and reactant flow through the anode, facilitating efficient electrochemical reactions within the cell.[4-6] Li, *et al.*[7] stated that SOEC and SOFC air electrodes have different optimum porosity values, 25-30% and 20-50% for electrolysis and fuel cell modes, respectively. Weng, *et al.*[8] reported that electrodes had to possess porosity within the range of 30-40% for optimum cell performance. Deng, *et al*.[9] concluded an optimal porosity between 27-44 % for anodes in SOFCs. Figure 2(H) highlights the region where the desired porosity could be achieved at different sintering temperatures, ranging from ~40% to ~20% at 1100°C and 1200°C.

Our research currently focuses on investigating the mechanical properties, particularly flexural strength, of porous ceramics with a target porosity of approximately 33%.

4. References

1. S.H. Ji, D.S. Kim, M.S. Park and J.S. Yun, “Sintering process optimization for 3YSZ ceramic 3D-printed objects manufactured by stereolithography,” *Nanomaterials*, **11** (1), 192 (2021); https://doi.org/10.3390/nano11010192.
2. ASTM Standard E112-13 (2021), “Standard Test Methods for Determining Average Grain Size,” ASTM International, West Conshohocken, PA, 2003; https://www.astm.org/e0112-13r21.html (accessed Jan. 2024).
3. W. Liu, *et al*., “3D printing of dense structural ceramic microcomponents with low cost: Tailoring the sintering kinetics and the microstructure evolution,” *J. Am. Ceram. Soc.*, **102** (5), 2257-2262 (2019); https://doi.org/10.1111/jace.16241.
4. S.C. Singhal and K. Kendall, *High Temperature Solid Oxide Fuel Cells: Fundamentals, Design and Applications*, Elsevier, 2003.
5. N. Hedayat, Y. Du and H. Ilkhani, “Review on fabrication techniques for porous electrodes of solid oxide fuel cells by sacrificial template methods,” *Renew. Sustain. Energy Rev*., **77**, 1221-1239 (2017); https://doi.org/10.1016/j.rser.2017.03.095.
6. S. Farhad, A.S. Fung and F. Hamdullahpur, “Effect of composite electrode microstructure on temperature distribution in solid oxide fuel cells,” *Electrochim. Acta*, **99**, 9-14 (2013); https://doi.org/10.1016/j.electacta.2013.03.056.

7. W. Li, Y. Shi, Y. Luo and N. Cai, "Theoretical modeling of air electrode operating in SOFC mode and SOEC mode: The effects of microstructure and thickness," *Int. J. Hydrogen Energy*, **39** (25), 13738–13750 (2014); https://doi.org/10.1016/j.ijhydene.2014.03.014.
8. F.-B. Weng, M.M. Dlamini, G. Jung and C.-X. Lian, "Analyses of reversible solid oxide cells porosity effects on temperature reduction," *Int. J. Hydrogen Energy*, **45** (21), 12170–12184 (2020); https://doi.org/10.1016/j.ijhydene.2020.02.157.
9. X. Deng and A. Petric, "Effect of anode porosity and pore size on electrochemical performance," *ECS Proc. Vol.: Eighth International Symposium on Solid Oxide Fuel Cells (SOFC-VIII)*, **2003-07**, 653 (2003); DOI: 10.1149/200307.0653PV.

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.
7. Quarter 7 (July-September 2023) Summary: *NASF Report* in *Products Finishing*; *NASF Surface Technology White Papers*, **88** (4), 17 (January 2024); Full paper: http://short.pfonline.com/NASF24Jan1.

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.