Development of Catalytic Porous Electrode Scaffolds for Mechanically-robust Hydrothermal Chimney Growth

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Introduction: Simulating prebiotic hydrothermal vents for lab-scale origin of life experiments uses chemical garden reactions that form self-assembled inorganic membranes via precipitation of metal silicates, (oxy)hydroxides, and/or sulfides (Barge at al., 2015). In certain chemical reaction systems, this nonequilibrium mineral precipitation generates wispy, fragile, porous structures with internal compartmentalization, suffering from non-epitaxial interfaces between multi-crystallite layers. The delicate nature of hydrothermal chimneys challenges *in-* and *ex-situ* characterization of the precipitated structures including adsorption and heterogeneous kinetics of prebiotic analytes on the chimney exterior (Barge at al., 2020; Koski et al., 1994; Lin, 2016; and Tivey et al., 1997). Further, this frustrates subsequent exchange of reactive fluids, fluid turbulence, or entrainment of microbes (Barge et al., 2020 and Jones et al., 2020). To stabilize these weak membranous hydrothermal chimneys during their growth, porous mineralogically-active ceramic electrodes may serve as scaffolding, thereby providing mechanical strength to withstand change of experimental conditions or extraction.

Advanced manufacturing techniques for scaffolding: Using vat stereolithography (SLA) and freeze casting, we have designed scaffolds composed of ceramics with nano/micro-mineral enrichment that serve as flow-through reactors to simulate hydrothermal chimneys. Silica (SiO_2)/alumina (Al_2O_3) fillers together with <1 µm diameter mineral powders, such as hematite and magnetite, are used within resins. In SLA, filled acrylate resins are fabricated layer-by-layer in the prescribed design by photopolymerization. Meanwhile, freeze casting involves the suspension of these pre-ceramic polymers in an organic solvent (e.g. cyclohexane) before controlled freezing of the solvent creating pore geometries, dependent on parameters including freezing rate and thermal gradient, followed by sublimation leaving the oxide scaffold behind (Naviroj et al., 2019). In both cases, the parts are then finished by pyrolysis at 900℃ under N_2. These manufacturing methods allow direct tunability of pore size and surface mineral content which may increase the chimney's adhesion to the scaffold. Their combination allows a range of scales in scaffold architectures from micron-to-millimeter in critical dimension.

Scaffolds offer improved mechanical resilience:

Material Selection: Silica/amorphous carbon, silicon (oxy)carbide (SiOC), and alumina ceramics were selected as end-use materials owing to their high elastic modulus, >100 GPa for SiOC and > 300 GPa for Al_2O_3 (Ming, 2019 and Formlabs, 2023), high thermal stability, and chemical inertness. Even under thermochemically reductive conditions – such as low partial pressures of oxygen with high partial pressure of hydrogen at high temperatures (Epifano and Monceau, 2023) – these materials are stable, making them ideal candidates for a nonreactive architecture.

Role of Architecture: Open-cell simple cubic lattices, inverse opal, and Voronoi cells were chosen in addition to interconnected extruded pores as the scaffold designs. These structural choices offer architectural strength, augmenting the base material properties (Montemayor at al., 2015 and Bechthold at al., 2017). They also provide channels and beams to act as conduits and barriers, respectively, for reaction front propagation, thereby permitting stable chimney growth within the scaffold and supporting membranous internal compartments.

In conclusion, we are exploring the application of materials science techniques for astrobiology. We target more mechanically robust hydrothermal chimneys via novel scaffolding approaches; future work will include scaffold incorporation into hydrothermal chimney experiments to observe their impact on morphology (if any), performing fluid exchange, and chimney-in-scaffold extraction.

References: Barge, L. M. et al. (2015) *Chemical Reviews*, 115(16), 8652-8703. Barge, L. M. et al. (2019) *PNAS*, 116(11),4828-4833. Barge, L. M. et al. (2020) *ACS Earth and Space Chemistry*, 4(9), 1663-1669. Barge, L. M. et al. (2020) *Journal of Geophysical Research: Planets,* 125(11), e2020JE006423. Bechthold, M. and Weaver, J. C. (2017), *Nature Reviews: Materials*, 2(12), 1-19. Epifano, E. and Monceau, D. (2023) *Corrosion Science,* 217, 111113. Shanti, N. O. et al. (2014) *Acta Materialia*, 71, 126-135. Formlabs (2023), *Alumina 4N TDS: Technical Ceramic with Extreme Performance*. Jones, J.P., et al. (2020) *Astrobiology*, 20(12), 1405-1412. Koski, R. A. et al. (1994) *Journal of Geophysical Research: Solid Earth*, 99(B3), 4813-4832. Lin, T. J. et al. (2016) *Geochemistry, Geophysics, Geosystems*, 17(2), 300-323. Ming, K. (2019) *Journal of Nuclear Materials*, 516, 289-296. Montemayor, L. Chernow, V., Greer, J. R. (2015) *MRS Bulletin* 40(12), 1122-1129. Naviroj, M., Voorhees, P. W., & Faber, K. T. (2017). Journal of Materials Research, 32(17), 3372-3382. Tivey, K. et al. (1997) *Geology*, 25(10), 931-934.