

GEO-ELECTRODES AND FUEL CELLS FOR SIMULATING HYDROTHERMAL VENT ENVIRONMENTS. L. M. Barge¹, F. C. Krause¹, J.-P. Jones¹, K. Billings¹, P. Sobron². ¹NASA Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena CA 91109 (laura.m.barge@jpl.nasa.gov), ²SETI Institute, 189 Bernardo Ave, Suite 200, Mountain View, CA 94043.

Introduction: Gradients generated in hydrothermal systems provide free energy for chemosynthetic life, are a consideration for present-day habitability on ocean worlds, and in the context of hydrothermal chimney structures may also be relevant to the origins of life on Earth [1,2]. Hydrothermal vents are similar in some ways to typical fuel cell devices: redox/pH gradients between seawater and vent fluid are analogous to the fuel cell oxidant / fuel reservoirs; the porous chimney wall is analogous to an ion-exchange membrane and is also a conductive path for electrons [3]; and the hydrothermal minerals are analogous to electrode catalysts. A fuel cell setup – with informed choices of materials and operating procedures – can be an effective simulator of geological environments containing redox-active materials, allowing for evaluation of energy present in a variety of systems [4]. We have performed fuel cell experiments and electrochemical studies to better understand the catalytic potential of seafloor minerals and vent chimneys, using samples from a black smoker vent chimney as an initial demonstration.

Methods: A mineral sample from a black smoker hydrothermal chimney (containing various metal [Zn,

Fe, Ni, Cu] sulfides / sulfur / Ca-sulfate) was used to create electrode ink by ball-milling the sample and suspending the powder in isopropanol/water/Nafion ionomer. This ink catalyst was then deposited onto glassy carbon electrodes as part of a three-electrode cell or onto a Nafion membrane to form a fuel cell membrane electrode assembly (MEA). The geo-electrodes / MEAs were tested in 1) a typical H₂/O₂ redox reaction and 2) in solutions representing the redox reactions that can take place at this kind of vent (sulfide oxidation / oxygen reduction [5]).

Results/Discussion: In voltammetry tests using electrode catalyst made of black smoker material, oxygen reduction was observed but hydrogen oxidation was uncertain, indicating that the geo-catalyst can function as the cathode half of a proton exchange membrane (PEM) H₂/O₂ fuel cell but not as the anode. The geo-catalyst was more stable in NaCl solutions simulating seawater. In voltammetry tests using NaCl + dissolved sulfide to simulate vent fluid, a multi-step sulfide oxidation process was observed. Fuel cells simulating vents were constructed using different ion-exchange membranes and liquid reactant reservoirs. These fuel cell experiments were able to simulate oxygen reduction that is proposed to occur in this black smoker system [5]; however, fuel cell tests revealed that sulfide oxidation is extremely facile even in the absence of the geo-catalyst on the fuel cell housing surface, indicating that other more inert materials would need to be chosen for constructing a more accurate fuel cell vent simulation. This PEM fuel cell experiment shows promise for correctly simulating a natural vent system, using either field samples or synthetic chimney material [6], and one major benefit of this is the possibility of using these techniques for simulating systems that lack accessible field analogs, e.g. geothermal vents on the early Earth that could have played a role in the emergence of life [1,2] or putative vents on Europa, Enceladus or other ocean worlds [7,8].

References: [1] Russell M. J. et al. (2014) *Astrobiology* 14:308-43. [2] Sojo V. et al. (2016) *Astrobiology* 16(2):1-17. [3] Nakamura R. et al. (2010) *ACIE* 49, 7692-7694. [4] Barge, L. M. et al. (2014) *Astrobiology* 14(3):254-270. [5] Yamamoto M. et al. (2013) *ACIE* 52, 41:10758-10761. [6] Barge L. M. et al. (2015) *JoVE* DOI:10.3791/53015. [7] Hsu H.-W. et al. (2015) *Nature* 519, 207-210. [8] Vance S. et al. (2007) *Astrobiology* 7, 987.

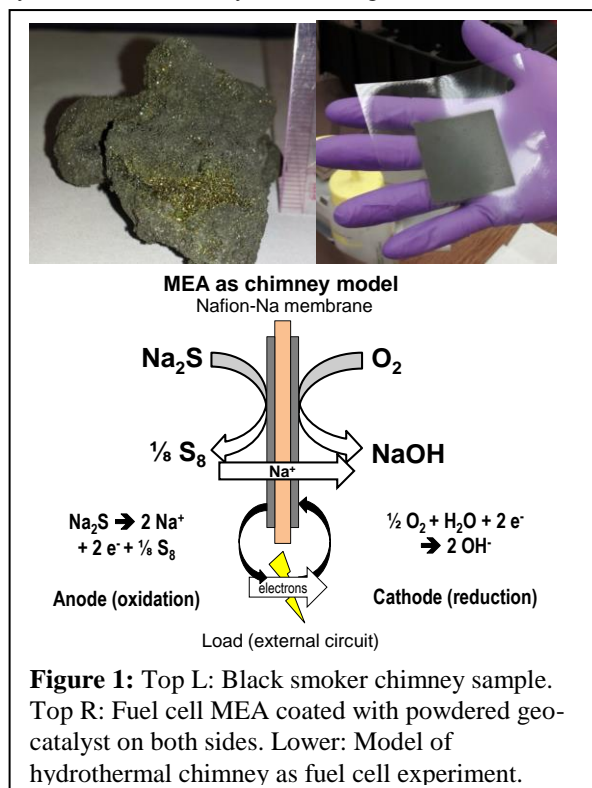


Figure 1: Top L: Black smoker chimney sample. Top R: Fuel cell MEA coated with powdered geo-catalyst on both sides. Lower: Model of hydrothermal chimney as fuel cell experiment.