

Abstract: We present our development of proton-conducting ceramic materials to synthesize methane and oxygen from CO₂ and H₂O feed streams. NASA seeks such technology to enable manned missions to Mars. The CO₂ and H₂O feedstocks are in abundant supply on The Red Planet; solar power could be harnessed to convert these feedstocks into fuel to sustain human life and enable permanent bases.

NASA's current approach features a two-stage process that starts with hydrogen synthesis through solar-driven water electrolysis using polymer-electrolyte membranes (PEM) at ~ 100 °C. Following H₂ synthesis, the product hydrogen is fed to a separate chemical reactor held at ~ 400 °C and mixed with CO₂ drawn from the Martian atmosphere. Within this reactor, a ruthenium catalyst promotes the Sabatier reaction to form methane:



This two-stage process joining a steam electrolyzer with a Sabatier reactor results in high conversion of CO₂ and reasonable rates of methane production. However, the PEM used for water electrolysis suffers from low efficiency, resulting in an energy-intensive fuel-synthesis process.

Our work seeks to combine these two processes into a single Sabatier Electrolyzer reactor based on proton-conducting ceramic membranes. Like PEMs, ceramic membranes transport reasonable rates of hydrogen, but do so at much-higher efficiency, decreasing power requirements. Additionally, protonic ceramics operate at temperatures that are more compatible with Sabatier chemistry (~ 400 °C). This enables integration of the catalyst with the electrolyzer, potentially simplifying the system, improving reliability, and increasing performance within a smaller package.

The Sabatier Electrolyzer concept is shown in the figure. Martian-derived H₂O and CO₂ are fed to the opposing electrodes of a protonic-ceramic electrolysis cell. The steam is electrolyzed (top), and as the product O₂ is exhausted from the cell, the product protons are driven across the protonic-ceramic membrane. These protons arrive at the fuel electrode, where they react with CO₂ to form methane and H₂O. The combination of processes can match the exothermicity of CO₂ hydrogenation with the endothermicity of H₂O electrolysis, promoting thermal balance and high efficiency.

This novel process intensification of mating water electrolysis with Sabatier chemistry brings many

questions. For example, do the protons emerging from the membrane at the fuel electrode directly react with CO₂ (as shown in the figure), or do they recombine to form H₂ that subsequently reacts with CO₂ within the nickel-laden fuel electrode to form CH₄? How can we better mate the operating conditions of the protonic-ceramic electrolyzer with those needed for Sabatier chemistry? What performance can NASA expect from a protonic-ceramic Sabatier Electrolyzer, in terms of electrical efficiency, methane production per unit mass, etc.?

CSM researchers have previously demonstrated encouraging results with proton-conducting ceramics for a number of applications, including electric-power generation and fuels synthesis. In this presentation, we will review our efforts to extend development of protonic-ceramic cells to the Sabatier Electrolyzer shown in Figure 1. The cells feature a BaCe_{0.2}Zr_{0.6}Y_{0.2}O_{3-d} (BCZY26) electrolyte, a Ni-BCZY26 fuel electrode support, and a BaCo_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1}O_{3-d} (BCFZY) steam electrode. Results will be presented for CO₂ conversion and CH₄ selectivity under electrolysis operation.

