The Fuel Cell Model of Abiogenesis:
A New Approach to Origin-of-Life Simulations

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Abstract

In this paper, we discuss how prebiotic geo-electrochemical systems can be modeled as a fuel cell and how laboratory simulations of the origin of life in general can benefit from this systems-led approach. As a specific example, the components of what we have termed the “prebiotic fuel cell” (PFC) that operates at a putative Hadean hydrothermal vent are detailed, and we used electrochemical analysis techniques and proton exchange membrane (PEM) fuel cell components to test the properties of this PFC and other geo-electrochemical systems, the results of which are reported here. The modular nature of fuel cells makes them ideal for creating geo-electrochemical reactors with which to simulate hydrothermal systems on wet rocky planets and characterize the energetic properties of the seafloor/hydrothermal interface. That electrochemical techniques should be applied to simulating the origin of life follows from the recognition of the fuel cell–like properties of prebiotic chemical systems and the earliest metabolisms. Conducting this type of laboratory simulation of the emergence of bioenergetics will not only be informative in the context of the origin of life on Earth but may help in understanding whether life might emerge in similar environments on other worlds. Key Words: Astrobiology—Bioenergetics—Iron sulfides—Origin of life—Prebiotic chemistry. Astrobiology 14, 254–270.

1. Introduction

Identifying the specific processes responsible for the emergence of life on Earth and then convincingly simulating these same processes in the laboratory are among the most intriguing challenges for contemporary biogeochemists. A large part of the difficulty is that plausible scenarios for the origin of life must not only account for the fundamental properties of life today but also for the geochemical conditions on early Earth through which life arose. These conditions are such that we only have patchy knowledge of them, and they present challenging engineering problems during attempts at simulation.

A primary process common to all extant life is the conversion of a pH gradient into energy-storing phosphate anhydride bonds via chemiosmosis across a semipermeable membrane. In prokaryotes, as well as in mitochondria, the “power plant” of eukaryotes, electric potentials across the membrane that induce a pH gradient between the membrane interior and exterior (i.e., the proton motive force) drive the fundamental energy generation mechanism for life (Mitchell, 1961; Jagendorf and Uribe, 1966; Harold, 1986). As in life today, the potential energy contained within these electron and proton gradients is transduced into useful chemical energy and stored in metastable energy currency molecules such as adenosine triphosphate (ATP) or inorganic pyrophosphate (PPi). It has been argued that the very first microorganisms were autotrophic; that is, they gained and assembled their building constituents from the simple molecules available to them on early Earth (e.g., H2, CO2, CH4, NH3/NH2, HPO2/C04, and HS/H2S) (Fuchs, 1989, 2011; Berg et al., 2010; Say and Fuchs, 2010). The electron transfer proteins involved in the generation of the proton motive force—many of which host inorganic metal sulfide–containing active centers—have been suggested to be among the most ancient catalysts (Eck and Dayhoff, 1966;
Microbes are, therefore, essentially performing the same chemical redox processes as those in ion-exchange membrane fuel cells (Mitchell, 1977; Barbir, 2005), and like fuel cells, biology uses proton and ion gradients to generate energy. In fact, recognition of this similarity within the fuel cell community has helped to implement the use of microbes, their redox-active enzymes, and even mitochondria themselves as components of electrodes for biofuel cells due to their excellent catalytic ability to transfer electrons and promote environmentally significant redox reactions (Arnold and Rechnitz, 1980; Heller, 1992; Chang et al., 2006; Arechederra and Minteer, 2008; Huang et al., 2012; Tran and Barber, 2012). Certain geochemical environments also constitute fuel cell–like systems, for example, at hydrothermal vents where electrical and pH potentials are generated at the interface between reduced hydrothermal fluid and oxidizing seawater (Baross and Hoffman, 1985; Russell and Hall, 1997, 2006; Martin and Russell, 2007; Yamamoto et al., 2013). In the hydrothermal vent example, the ambient geochemical potentials can be maintained and mediated across physical boundaries, for example, electrically conductive biofilms, sediments, or an inorganic chimney precipitate (Ludwig et al., 2006; El-Naggar et al., 2010; Nakamura et al., 2010a, 2010b; Yamamoto et al., 2013). A second geological example of fuel cell–like behavior that is believed to have been of significance within early Earth environments is galvanic corrosion of iron-nickel alloys (associated with meteoritic infall) from contact with seawater, which can in principle establish pH/Eh gradients (Bryant et al., 2013).

Because life universally depends on pH/Eh gradients to drive metabolism, geological environments that already generate similar electrochemical energy gradients are of interest for origin-of-life studies. One such example is hydrothermal vents, which can be produced by magmatic activity (e.g., black smokers) or water-rock chemistry (e.g., serpentinite-hosted alkaline vents). Alkaline hydrothermal vents produced by serpentinization (the process of olivine/pyroxene oxidation via seawater interaction in a series of exothermic reactions) are of special interest to the origin of life, as they can generate a very alkaline hydrothermal effluent and, thus, an ambient pH gradient in addition to an electrical potential difference across the fluid interface (Baross and Hoffman, 1985; Russell and Hall, 2006; Martin et al., 2008; Russell et al., 2010; Lane and Martin, 2012). Serpentinization is likely to have progressed on early Earth (Russell et al., 1989; Sleep et al., 2011; Arndt and Nisbet, 2012) and may have been active elsewhere in the Solar System, for example, on early Mars, Europa, or other icy moons with a water-rock interface (Vance et al., 2007; Ehlmann et al., 2010; Wray and Ehlmann, 2011; Michalski et al., 2013), possibly providing an environment for emergent prebiotic chemistry.

The operations of extant life are analogous to those of a fuel cell, and some version of the fundamental components that make the biological fuel cell function (ATP-synthase, ion-selective membranes maintaining pH/Electrical gradients, the electron transport chain) was also likely present in LUCA, the last universal common ancestor (Gogarten et al., 1989; Martin and Russell, 2007; Mulkidjanian et al., 2007; Schoepp-Cothenet et al., 2013). Because we consider that LUCA also had these basic fuel cell properties (Russell and Hall, 1997; Nitschke and Russell, 2009; cf. Huang et al., 2012; Lane and Martin, 2012), we suggest that some key steps at the origin of metabolism may then be simulated experimentally within the context of the electrochemical gradient architecture of a fuel cell. As life is an example of a far-from-equilibrium biological system, which presumably emerged from a far-from-equilibrium geological and geochemical system, it seems logical that a far-from-equilibrium chemical system such as a fuel cell may provide an effective link between the two.

We set out to examine whether the fuel cell–like properties of certain geochemical environments, such as seafloor interfaces and hydrothermal vent systems, could be simulated in out-of-equilibrium electrochemical experiments and ultimately modeled in the laboratory as a fuel cell. In a geological/geochemoical fuel cell scenario, some mineral or other inorganic component would be required to act as an electrocatalyst as well as an ion transfer “membrane” that separates contrasting chemical reservoirs. Depending on the scenario, this component could be a conductive mineral, gel, or other porous material. For our preliminary experiments, we chose to focus on (i) Fe sulfides and (ii) Fe-Ni phases within iron meteorites. Both of these are viewed as being potential electron transfer catalysts relevant for protometabolic reactions and are considered to be readily available and accessible on early Earth (Williams, 1961, 1965; Eck and Dayhoff, 1966; Russell et al., 1994; Bryant et al., 2009, 2013; Nitschke and Russell, 2011). Metal sulfides in particular constitute an important part of the environmental fuel cell in modern hydrothermal vent systems as they facilitate transfer of electrons (Nakamura et al., 2010b). The nature of mineral precipitation in a gradient is also significant, as the chemical disequilibrium can result in complex precipitate structures such as hydrothermal “chemical garden” chimneys (Haymon et al., 1983; Russell et al., 1989, 1994; Ludwig et al., 2006) that may exhibit electrochemical and ion-transfer capabilities (Ayalon, 1984; van Oss, 1984). To model these conditions in the laboratory, an iron sulfide electrocatalyst material was synthesized by separating an acidic, Fe$^{2+}$-containing solution and an alkaline, sulfide-containing solution across a permeable barrier to form a self-assembling precipitate membrane in a gradient. This simulated geological precipitate separated two contrasting solutions and could mediate gradients, as might occur in a natural far-from-equilibrium system such as chimney growth at a hydrothermal vent. Electrochemical experiments also were conducted by using geological analog materials (both synthetic and field samples) as catalysts, and a proton exchange membrane (PEM) fuel cell apparatus was constructed to simulate an electrochemically active geochemical interface. The fuel cell represents a holistic chemical system that is well understood, amenable to computational modeling, and open to sophisticated analytical diagnostics. This systems approach has not yet been exploited experimentally within the sphere of abiogenesis and offers a potentially powerful theoretical and experimental model through which to explore such emergent physicochemical systems. These experimental techniques
can be applied to a variety of geochemical systems or analog materials and may even be used to simulate energetic processes at seafloor interfaces on other planets as well as to determine whether prebiotic chemistry would be possible on other wet, rocky worlds.

2. Examples of Fuel Cell-like Systems in Biology and Geology

To envision experimental ways by which to test prebiotic chemistry within an electrochemical framework, it is useful to define and constrain the functional parts of the natural fuel cells of geology and biology, as well as a proposed prebiotic fuel cell (PFC) that may have powered inorganic and organic redox reactions on early Earth.

Fuel cells are primarily composed of an anode (the surface where oxidation occurs), a cathode (the surface where reduction occurs), and an ion-conducting electrolyte that physically separates reservoirs containing the fuel and oxidant (Haile, 2003a, 2003b). The physical setup of the fuel cell that separates two chemically distinct reservoirs is essential, for it is this chemical/redox disequilibrium—chemical gradients maintained over some distance—from which electricity is ultimately produced. The essential components include the electrolyte, which physically separates the fuels and oxidants, allowing a voltage gradient to be maintained; the electrodes, which facilitate oxidation/reduction and contain catalytic materials; and the fuel (electron donor) and oxidant (electron acceptor), which transfer electrons to and from the electrodes.

Mitochondria, the free energy factories of animal cells, are very efficient electrochemically, and they and their associated enzymes have been successfully used as electrodes in manmade fuel cells (e.g., Arechederra and Minteer, 2008). As in a PEM fuel cell, the flow of protons and electrons is spatially separated in mitochondria, and life has evolved precise chemical means by which to harness the energy present in these potential gradients. The lipid bilayer membrane is the capacitor that separates contrasting chemical environments, and the electrodes of mitochondria are the ends of a series of electrochemically connected enzyme complexes within the inner membrane, together known as the electron transport chain. The iron-nickel-sulfide–containing centers of the enzymes act as anodes and cathodes (Berg and Holm, 1982; Baymann et al., 2003; Vignais and Billoud, 2007), while the membranes—capable as they are of selective ion transport—maintain chemical disequilibrium (Lane and Martin, 2012). Derived from proteobacteria, the mitochondria bear certain similarities to chemiosmotic LUCA (Yang et al., 1985; Martin and Müller, 1998; de Paula et al., 2013). LUCA’s biological battery would have had some similar functional parts, such as the complex I, referred to as the “steam engine of the cell” by Efremov and Sazanov (2011), that drives protons to the periplasm through redox disequilibria. These protons form a pH gradient due to the disequilibrium between membrane exterior and interior and drive ATP synthase—the rotary biomolecular motor—to make ATP (Yoshida et al., 2001; Branscomb and Russell, 2013).

A geological fuel cell phenomenon also can emerge without biological mediation at seafloor interfaces, for example, in hydrothermal vents produced either by magmatic activity or by water-rock chemistry. High-temperature hydrothermal alteration on oceanic spreading ridges can produce a hot (>350°C) acidic hydrothermal fluid driven by magmatic intrusion that fuels black smokers, named after the black particles that form as the rapid temperature/pH change induces precipitation of metal sulfides at the fluid interface. In the absence of magmatic heating, reducing hydrothermal fluids can also be produced by serpentinization, a process in which seawater permeates through fractures in the Fe/Mg-silicate ocean crust and produces an alkaline, H2- and CH4-enriched, moderately hot (≈100–200°C) hydrothermal fluid (Russell et al., 1989; Kelley et al., 2001, 2005; Bradley and Summons, 2010; Charlou et al., 2010; Klein et al., 2013), even in low-temperature exhalations (Neal and Stanger, 1983; Coveney et al., 1987; Etiope and Sherwood-Lollar, 2013; Etiope et al., 2013).

Both black smoker and alkaline vents can produce chimney precipitates where hydrothermal fluids feed back into the ocean, and these naturally occurring mineral precipitates are significant in that they provide a semipermeable and semi-conducting barrier between the two contrasting fluids. The redox-active fluid interface of a hydrothermal vent consists of fuel/oxidant reservoirs separated by an inorganic mineral precipitate and constitutes a naturally occurring fuel cell that does not depend on biological processes to function. The inside and outside surfaces of the hydrothermal chimney could be considered as anode and cathode, respectively. Depending on composition and environmental conditions, the chimney itself may be able to catalyze the oxidation of hydrothermal fuels and conduct resulting electrons to seawater oxidants. The fuel cell–like properties of hydrothermal vents have been directly demonstrated in field studies of black smoker vents, in situ by harnessing the electrical current produced by the vent to power a small device on the seafloor (Yamamoto et al., 2013), as well as in the laboratory, where it has been demonstrated that black smoker chimney material is electrically conductive and capable of catalyzing redox reactions (Nakamura et al., 2010b).

It is also perhaps pertinent to the PFC model that, as pure metals and metal alloys are frequently found to be highly efficient electrocatalysts (Chen et al., 2011), such materials were probably geologically present within the Hadean period through the reducing power of serpentinizing vents (e.g., awaruite, Ni$_3$Fe; Ulrich, 1890; Frost, 1985; Klein and Bach, 2009) and as Fe-Ni meteorite deposits during the late heavy bombardment (Buchwald, 1977; Cockell, 2006). The corrosion of metals and metal alloys by an electrolyte such as seawater can give rise to a localized fuel cell–like system: anodic oxidation of Fe to Fe$^{2+}$ with concomitant cathodic reduction of, for example, SO$_4$$^{2-}$ to elemental S or S$^{2-}$; H$^+$ to H$_2$; or NO$_3^-$ to NO$_2^-$ (Bryant et al., 2013)—each of which could, in principle, establish localized pH/Eh gradients.

3. Creating a Fuel Cell Model of a Prebiotic Hydrogeological System

The energetic “essence” of extant anaerobic life could be viewed as quite similar to a fuel cell, in that ion gradients and electron potentials maintained across a membrane produce energy as long as fuels and oxidants are supplied. The sediment/water or hydrothermal/ocean interfaces in modern
marine systems also can constitute naturally occurring fuel
cells, deriving from the electrochemical cell of Earth and its
atmosphere and mediated by microbes acting as redox cat-
ystics. This has led to the proposal that ion/electron poten-
tials also were the driving forces for life’s origin and that
these gradients were initially provided by the naturally oc-
curring pH/Eq potentials in alkaline hydrothermal vents
(Russell and Hall, 1997; Russell et al., 2010). This alkaline
hydrothermal origin-of-life model can be generalized to any
wet rocky world with a chemically similar water-rock in-
terface (Russell et al., 2014), so we chose to develop our
electrochemical/fuel cell model using alkaline vents as one
example of a hydrogeological origin-of-life scenario that
could benefit from this concept. Similar fuel cell models
also could be applied to simulating electrochemically active
water-rock interfaces on early Mars, early Venus, or the icy
moons of Jupiter and Saturn.

Earth’s oceans 4 billion years ago are thought to have
been anoxic, mildly acidic (pH ∼ 5–6 due to dissolved
atmospheric CO2, NO, and ephemeral SO2), and rich in
Fe2+; and they could have contained Ni2+, Mn2+, phos-
phates, nitrate, nitrite, and some ferric and manganese ions
(Macleod et al., 1994; Russell and Hall, 1997; Hagan et al.,
2007; Martin and Russell 2007; Ducluzeau et al., 2009;
Mloszewska et al., 2012; Nitschke et al., 2013). The hy-
drothermal fluids produced by serpentinization would likely
have been similar to modern-day hydrothermal fluids: al-
aline, containing some silicate, trace Mo and W, and dis-
solved H2 and CH4 along with formate and a range of
hydrocarbons (Proskurowski et al., 2008; Konn et al., 2009;
Lang et al., 2010, 2012; Mielke et al., 2010; Charlou et al.,
2010). It is also thought that ancient hydrothermal springs in
serpentinizing systems would have contained millimolar
levels of sulfide from dissolution of crustal sulfide minerals,
as determined from laboratory reactor experiments simu-
lating serpentinization in a Hadean system (Mielke et al.,
2010, 2011). Vents driven by serpentinization produce rela-
tively low-temperature fluids compared to the scalding
environment of black smokers, but between them, hyd-
thermal vent systems on early Earth could have contributed
many of the fuels and materials that are thought to be re-
levant for an autogenic/autotrophic emergence of life. The
interfacing of alkaline hydrothermal fluids and seawater on
early Earth might have produced a variety of inorganic
precipitates within the ambient geochemical/electro-
chemical gradients, among them, silica gel, ferrous/ferric
oxyhydroxides, and transition metal sulfides (Russell and
Hall, 1997). Hydrothermal precipitates formed by serpen-
tinization on early Earth might therefore have had mineral
compositions and electrochemical properties in some ways
similar to modern black smoker chimneys, for example,
conductive iron sulfide minerals that catalyze redox reac-
tions. Thus, electrochemical studies of modern black
smokers (e.g., Nakamura et al., 2010b; Yamamoto et al.,
2013) may also be relevant for understanding the energetics
of hydrothermal vent fuel cells on early Earth.

A putative Hadean hydrothermal vent with a chimney
structure would have operated somewhat like a flow-through
fuel cell. The contrasting reservoirs of reduced, H2/CH4-
containing hydrothermal fluid and the relatively oxidized
(containing minor concentrations of FeII and dissolved
NO), CO2-rich ocean would have been separated by a pre-
cipitate of mixed composition, containing material such as
carbonates, silicates, and iron and other transition metal
sulfides and mixed-valence layered iron “double” oxy-
hydroxides (Russell et al., 2014; Fig. 1). Transition metal
sulfides are one of several possible components of a prebi-
otic hydrothermal chimney, but as one of the more elec-
trochemically active materials likely to be present, it is
useful to characterize iron sulfide chimney growth and
electrochemistry in the laboratory, which various studies
have pursued (Russell et al., 1989; Mielke et al., 2010,
2011; McGlynn et al., 2012; Barge et al., 2014). Many
properties of iron sulfide precipitates relevant to a far-from-
equilibrium geological system have been experimentally
determined. For example, when initially precipitated be-
tween contrasting solutions, self-assembling iron sulfide
membranes are capable of generating an electrical potential
of ∼0.6 to 0.7 V and maintaining the pH gradient between
the hydrothermal and ocean solutions (Fittness et al., 2003;
Russell and Hall, 2006; Barge et al., 2014). The precipitates
produced in out-of-equilibrium experiments have a complex
structure at the microscale; membranes vary in thickness
from ∼5 to ∼100 μm, exhibit and comprise a mix of iron
sulfides and iron oxyhydroxides/silicates, and can also in-
corporate dissolved ions such as other transition metals and
phosphates (Mielke et al., 2011; Barge et al., 2012, 2014;
McGlynn et al., 2012; Barge and Kanik, unpublished data).

In a hydrothermal system with a chimney structure, the
precipitate could facilitate diffusion of ions and electron
conduction (Nakamura et al., 2010b); thus, it could function
as a selectively permeable electrolyte membrane between
hydrothermal fuels and seawater oxidants. In a fuel cell
concept of prebiotic alkaline hydrothermal vents, the anode
and cathode would be the interior and exterior chimney
mineral surfaces, respectively. The exterior and interior of a
chimney could have different mineral compositions, since
chemical garden–like structures tend to exhibit composi-
tional variations across the membrane reflecting the chem-
ical gradients in which they precipitate (Pagano et al.,
2006; Russell and Hall, 2006; Cartwright et al., 2011; Barge
et al., 2012). Though a hydrothermal chimney would likely
also contain components such as silica gel or carbonate, the
ability of the “electrodes” to drive redox reactions would
probably be dependent on the presence of electrocatalytic
minerals such as metal sulfides and oxyhydroxides (cf.,
Arrhenius, 2003; Antony et al., 2008). Minerals such as
mackinawite (FeS) and greigite (Fe3S4) are electrically
conductive, can behave as capacitors, and are thought to be
catalytically active in organic reactions (Huber and Wäch-
tershäuser, 1997; Rickard et al., 2001). These iron sulfide
minerals also are structurally similar to the Fe2S3 and FeS
groups in metalloenzymes that catalyze redox reactions in
biology, a similarity that has led to the suggestion that these
metalloenzyme centers originally derived from inorganic
hydrothermal minerals (Russell and Hall, 1997, 2006;
Rothery et al., 2008; Nitschke et al., 2013). In a putative
prebiotic hydrothermal fuel cell, transport of electrons from
fuel to oxidant could be mediated by a series of smaller
redox steps, as in biological systems. Within this scenario,
the fuels and oxidants would be indefinitely replenished as
long as serpentinization remained active, which is envisaged
for modern alkaline hydrothermal systems to last for over
one hundred thousand years (Ludwig et al., 2011). The
chimney membranes themselves could be continuously renewed as the hydrothermal fluids produced by serpentinitization continue to rise and interface with the ocean, feeding through and possibly disaggregating older membranes.

4. Experimental Studies: Exploiting Electrochemical Techniques and Fuel Cells as Planetary Geology Test Beds

The large body of fuel cell work in which enzymes, mitochondria, or microbes are used as electrocatalysts is testament to the importance of charge and concentration gradients in biology. Because both hydrogeological environments (e.g., vents) and biological cells (at least, in their free energy generation mechanisms) can be conceptualized as fuel cells, it is reasonable to pursue hydrothermal origin-of-life experiments in a setup that preserves these fundamental aspects of pH and electrochemical gradients across a membrane. To this end, we conducted preliminary experiments to simulate hydrogeological systems with electrochemical gradients and using geological materials as electrode catalysts. We illustrate how these methods can be used to simulate geochemical free energy interfaces and test hypotheses regarding the transition to bioenergetics. It is our intention to broaden these initial studies of simulated sea-floor/hydrothermal interfaces to explore application of similar techniques to other hydrogeological environments, such as galvanic corrosion of iron meteorites or water/rock interfaces on other planets, within the framework of a fuel cell reactor. We envisage the results presented here to be preliminary indications of possible value in the model we propose.

4.1. Electrochemical studies of simulated hydrothermal precipitates

Though an ancient hydrothermal chimney would have had a heterogeneous composition, some of the most electrochemically relevant minerals thought to be formed in this system are iron and iron/nickel sulfides. To investigate the electrochemical properties of metal sulfide minerals that could be formed at alkaline vents on early Earth, we precipitated inorganic membranes in out-of-equilibrium solution interface experiments (Fig. 2; Filtness et al., 2003; Barge et al., 2014). We interfaced contrasting solutions that represent the dissolved Fe²⁺ in the acidic primordial ocean (added as dissolved FeCl₂·4H₂O) and dissolved sulfide in the alkaline hydrothermal fluid released from crustal sulfide minerals (added as dissolved Na₂S·9H₂O). When interfaced, these solutions self-assembled into mineral precipitates in the same manner as the injection chemical garden experiments used previously to simulate Hadean hydrothermal chimney precipitates (Mielke et al., 2011; Barge et al., 2012, 2014). However, we have found that a glass fuel cell setup yields a more structurally stable membrane precipitate that can be used in subsequent electrochemical experiments (Barge et al., 2013, 2014). We have previously formed iron sulfide membranes (and chimneys) using various Fe²⁺ and sulfide concentrations and have found that, although membranes can be formed by using geologically realistic
millimolar concentrations over 3–4 days, more robust membranes form over shorter timescales when using higher (≈50 mM) concentrations, and these still preserve the out-of-equilibrium nature of the precipitates. Therefore, we used higher reactant concentrations in this study to form precipitates on shorter timescales that are reasonable for laboratory experimentation and to generate more precipitate material for use as an electrocatalyst. We recognize that, in a natural system, similar precipitates might take much longer to form from the dilute Fe$^{2+}$- and sulfide-containing fluids.

4.1.1. Formation of membranes simulating hydrothermal chimney walls. A synthetic porous membrane template was clamped between two fluid reservoirs in a two-chamber glass membrane fuel cell apparatus (Adams & Chittenden glassware, with high-temperature clamp stable up to 150°C). Most experiments were performed by using dialysis tubing (Fisher, 3500 MCW) as the precipitation template, but conductive carbon cloth (Sigracet, hydrophilic, no microporous layer) was also tested as a template material. The iron and sulfide solutions were added to the half-cells respectively, and the cell was kept anoxic throughout with constant N$_2$ purging and allowed to react for 24 h at room temperature. High-resolution imaging and chemical analysis were carried out on the iron sulfide membranes by using an environmental scanning electron microscope with an attached energy-dispersive X-ray tube. The electrical potential generated across the inorganic membrane as it precipitated was recorded over the course of experiments by an Agilent LXI Data Acquisition/Data Logger Switch Unit with electrodes placed in each cell. pH measurements were recorded with an Excel XL20 pH/conductivity meter (Fisher Scientific) with temperature calibration. The membranes formed were used in subsequent electrochemical experiments, described below.

4.1.2. Membrane potential tests. We conducted membrane potential tests in which an iron sulfide membrane was allowed to precipitate for 24 h, followed by removal of the iron and sulfide solutions. The membrane and both half-cells were carefully rinsed with ddH$_2$O; then NaCl or KCl salt solutions of varying concentration were added to both sides of the precipitated membrane. Salt concentrations were 10× greater on the “formerly alkaline” side than on the “formerly acidic” side, and concentrations between 10 mM and 1 M were tested for both NaCl and KCl. Electrodes were placed several millimeters from either side of the membrane surface to record the membrane potential. In previous studies, this technique has been shown to generate concentration-dependent membrane potentials across inorganic precipitate membranes in many different chemical systems including sulfides (e.g., of Hg, Sn), although iron sulfide measurements were not reported (Beg et al., 1977, 1978, 1979; Sakashita and Sato, 1977; Malik et al., 1980; Ayalon, 1984; Siddiqi and Alvi, 1989; Kushwaha et al., 2001; Beg and Matin, 2002).

4.1.3. Membrane galvanostatic tests. We conducted galvanostatic tests in which an electrical current was applied across an iron sulfide membrane after it had formed (Honig and Hengst, 1970). Half-cells were filled with acidic FeCl$_2$·4H$_2$O solution and alkaline Na$_2$S·9H$_2$O solution, respectively, and a dialysis membrane was clamped between the two reservoirs. Two electrodes were placed in each cell: one in the bulk solution to apply current and one very close (2–3 mm) to the membrane to measure membrane potential. After the membrane had precipitated for 24 h, a current of ±0.75 mA/cm$^2$ was applied across the membrane, and the resulting membrane potential relative to the rest potential was measured. The measurement also was repeated after both half-cells had been emptied and refilled with 0.1 M NaCl solution.

4.1.4. Voltammetry studies. To investigate the ability of iron sulfide chimney precipitates to facilitate electron transfer from hydrothermal reductants to seawater oxidants in a prebiotic hydrothermal system, we applied simulated hydrothermal iron sulfide–containing precipitate membrane material as a catalyst on a glassy carbon electrode (GCE). Cyclic voltammetry half-cell experiments were conducted in...
which the GCE+ catalyst was characterized in a Hadean ocean simulant containing oxidants of interest to the origin of life in serpentinitizing systems. In this experiment, a Fe/S precipitate membrane was formed in the fuel cell apparatus shown in Fig. 2, and after 24 h the membrane was removed, rinsed with ddH₂O, and dried under N₂. The dried precipitate was removed from the dialysis membrane template and attached to a GCE with conductive carbon tape. Potential from ±1 V was applied (relative to Ag/AgCl, using a Pt counter electrode) in a solution representing bicarbonate as an electron acceptor in the Hadean ocean (20 mM NaHCO₃ + 0.6 M NaCl, titrated to pH ~ 5). A control was performed such that no FeS catalyst was applied to the working electrode, but ground FeS particles (Sigma) were stirred into the simulated ocean while potential was applied. Other controls had no FeS in the system. Experiments also were performed in which carbon cloth was used as the membrane separator in the two-cell precipitation apparatus described above, so that Fe/S membranes were precipitated directly onto the carbon cloth and pieces of the Fe/S-covered cloth (5 mm × 50 mm) could be used directly as working electrodes in voltammetry studies. Controls were also performed with plain carbon cloth (with no Fe/S) as working electrode.

4.2. Fuel cell reactors simulating prebiotic geo-electrochemical systems

4.2.1. Fuel cell design rationale. An origin-of-life fuel cell experiment designed to test a hydrogeological system on early Earth or any wet rocky planet might involve a combination of techniques: synthesizing simulated mineral catalysts in out-of-equilibrium systems (as in Barge et al., 2012, 2013, 2014; Mielke et al., 2010, 2011); electrochemical studies of simulated precipitate materials to characterize their utility as electrocatalysts; and the use of these simulated prebiotic catalysts to create catalytic electrodes for use in a fuel cell. There are various types of fuel cell experiments that could be informative in this regard. Imitating the design of microbial fuel cells (MFCs), where the catalytic electrodes are submerged in two liquid reservoirs and separated by an ion-exchange membrane, would allow for testing of different fluid chemistries and dissolved ionic, as well as gaseous, electron donors and acceptors. MFC-type experiments would also lend themselves well to testing other relevant biological components as catalysts, such as individual enzymes or organisms. A geo-electrochemical system also could be simulated by a proton exchange membrane fuel cell (PEMFC), which could use gaseous reductants/oxidants under higher pressure or temperature, with the simulated geological catalysts embedded in the gas diffusion layers (GDLs) within the membrane electrode assembly (MEA). Either way, the modular engineering arrangement of fuel cell components makes for a convenient planetary geology test-bed system in which components, such as the ion-exchange membranes, electrodes and catalysts (or electrolyte assembly unit), and the anode/cathode reactant feeds, may be substituted by materials more closely connected to geological environments. For example, rather than a commercial GDL catalyst layer, one could substitute simulated hydrogeological precipitates similar to those described above. This type of experiment is not limited to simulating hydrothermal vent environments; other geological electrochemical processes of interest could be explored in a similar experimental setup, for example, as mentioned in Section 1 above, the electrochemical corrosion of meteorites on early Earth (Bryant et al., 2009). Field samples of catalytic minerals derived from reduced Fe/Ni in meteorites, which have been previously proposed to assist with early phosphorus chemistry (Pasek and Lauretta, 2005; Pasek et al., 2013), could be treated in the same way as hydrothermal precipitates in the GDL electrocatalyst layers (see below).

We conducted some preliminary proof-of-concept tests, using a PEMFC to simulate the catalytic action of geological mineral catalysts in a far-from-equilibrium system. A sample experimental arrangement for a PEMFC that simulates a geo-electrochemical system is shown in Fig. 3. In our preliminary tests, a commercial proton-exchange membrane and two GDLs containing electrocatalysts were sandwiched between two composite graphite bipolar plates, and the fuel cell was fed with humidified hydrogen (to represent hydrogen
produced by serpentinization) and air at the anode and cathode sides, respectively. We examined the potential for efficient carbon-black-deposited platinum electrodes to be replaced by geological materials, in this case Fe-Ni alloys present within iron meteorites, where taenite and kamacite are the dominant phases. While these materials may at first glance appear incompatible with terrestrial minerals, there is support for them to have contributed a significant component of the early Earth lithosphere (Pasek and Lauretta, 2008), and they are closely related to the hydrothermal Fe-Ni mineral, awaruite (Klein and Bach, 2009). Most importantly, these meteorite samples represent a proof of concept for fabricating geologically analogous GDLs or electrodes for a planetary geology fuel cell reactor by using field samples rather than synthetic catalysts. Such a procedure could be applied to other field samples of interest, for example, samples of hydrothermal precipitates, serpentinite, metal sulfides, or other minerals that might be important in a prebiotic system.

4.2.2. Preparation of geological fuel cell catalysts. The Fe-Ni “geological electrocatalyst” was prepared by using shavings from the coarse octahedrite, group IAB-sLL Toluca meteorite that has a mean composition of 91% Fe and 8.1% Ni (Fig. 4). This geological sample was ball-milled to an average particle diameter of ca. 5 microns before being dispersed in ethanol, sonicated in an ultrasonic bath for 10 min, mixed with Nafion polymer binder, and then sprayed onto a GDL. For both electrodes, the amount of catalyst required was calculated based on a 1.0 mg/cm² catalyst loading within an 11.56 cm² active area. Both the cathode and anode electrodes were positioned on the faces of the catalyst-coated Nafion membrane and hot-pressed (with a hydraulic press) to form a unit of MEA. The required amount of the catalyst was first ultrasonically mixed for a few seconds with a few drops of deionized water in order to break the catalyst powder into small pieces and prevent the catalyst from being deactivated when blending it with the dispersion agent, ethanol. A calculated amount of 50 wt % ethanol based on 15 mL ethanol per 50 mg catalyst was added to the wet catalyst, and the resulting mixture was ultrasonically blended for about 3 min. The resulting blend was then mixed with a 5 wt % Nafion solution (Sigma Aldrich) based on a loading of 0.1 mg Nafion/cm². The Nafion solution is added to create an ionic phase for proton transport from the anode to cathode. This final mixture was ultrasonically blended for 15 min to form what is normally known as an “electrode ink.” The electrode ink was then manually sprayed onto the surface of the GDL that was mounted on a PTFE plate heated to 80°C to evaporate the alcoholic components, until the desired 1.0 mg/cm² catalyst loading was reached.

4.2.3. Preparation of membrane electrode assembly. A mixture of 5 wt % Nafion solution, calculated based on 0.5 mg Nafion/cm², and acetone (about 3–5 mL) was sprayed onto the surface of the catalyzed GDL to enhance the contact between the catalyst layer and the Nafion membrane in the MEA being fabricated. The N115 Nafion membranes were pre-treated before being used in MEA fabrication by heating at 80°C in 2 wt % hydrogen peroxide solution for 1 h, rinsing several times with deionized water, heating in 1 M sulfuric acid at 80°C for 1 h, and finally rinsing several times with deionized water. Both the cathode and anode electrodes were positioned on the faces of the Nafion membrane and hot-pressed with a hydraulic press at 130°C and 50 kg/cm² for 3 min to form a unit of MEA.

4.2.4. Assembly and operation of the PEMFC. A single PEMFC was assembled by sandwiching the MEA between two composite graphite bipolar plates (Bac2) with an 11-turn and single-pass serpentine flow channel (2 mm × 2 mm, with a rib of width 0.8 mm). The PEMFC was placed between two copper end plates and connected to an in-house fuel cell test station. The fuel cell was maintained at room temperature and fed with hydrogen at the anode side and air at the cathode side (Fig. 5). The flow rates of both hydrogen and air were kept constant, equivalent to a stoichiometry of 2 calculated based on a 500 mA/cm² current density. Dry hydrogen and air were fully humidified by flowing through bubbler-type humidifiers. The pressures of the inlet and outlet gases were 1 and 0 barg, respectively. Electrochemical tests were performed with a Gamry Reference 3000 potentiostat/galvanostat.
5. Results

5.1. Electrochemical characterization of simulated hydrothermal precipitates

When the contrasting acidic/iron (ocean simulant) and alkaline/sulfide (hydrothermal simulant) solutions were added to the two-chamber cell, they interfaced across the porous separating barrier and immediately began to produce a self-assembling iron sulfide-containing precipitate film in/on the template. The characteristics of this inorganic membrane precipitate varied depending on compositions of the two solutions and on the nature of the membrane template material, but commonly a complex landscape of micron-scale crystal structures formed (Fig. 6A)—not unlike the crystal morphologies observed in the interior membranes of chemical gardens formed in injection experiments (Cartwright et al., 2002, 2011; Barge et al., 2012). When dialysis tubing was used as the template, the membrane precipitate formed within the pores and also on the surface of the dialysis tubing. Membranes precipitated on dialysis tubing proved to be ideal for electrochemical characterization within the original precipitation apparatus, since the dialysis template is only permeable to ions and solution mixing was completely prevented. Thus, precipitates only formed on the template separating the two solution reservoirs, not in either solution. Dialysis templates also yielded membranes that were structurally stable enough to enable gentle rinsing and emptying/refilling of solutions, and when removed from the cell, the precipitate was a flaky solid film that could be easily dried and removed from the dialysis tubing for later use as a catalyst. Carbon cloth was much more porous than the dialysis tubing, and when used as a precipitation template, it did not prevent solution mixing as effectively. Thus, in the precipitation fuel cell apparatus where carbon cloth was used as the separator, the two solutions often mixed near the interface (forming Fe/S precipitates in the bulk solutions as well as on the carbon cloth), and it was not possible to do electrochemical experiments with the membrane still in situ. We also found that it was necessary to pretreat the carbon cloth by wetting it with ddH2O, rinsing to remove extraneous carbon material that was not contained within the woven fibers, and applying FeCl2•4H2O and Na2S•9H2O solutions directly to the cloth to form a “starter” precipitate in the pores before placing it between the two solution reservoirs. In any case, using carbon cloth caused the FeS precipitate to form on the carbon cloth fibers (Fig. 6B); and because carbon cloth itself is conductive, a piece of the cloth containing FeS precipitate could be directly used as a working electrode.

We observed that, even in a system containing only iron and sulfide, these self-assembling inorganic membranes were able to mediate chemical/pH gradients for several days, as observed by monitoring the pH of the acidic cell. The membranes also generated a diffusion potential of ~300–600 mV as they formed, depending on experimental conditions, as was observed in a similar experiment by Filtness et al. (2003). This potential declined over several days as ions diffused through the membrane, eventually reaching equilibrium. When the iron and sulfide solutions were removed after a membrane had precipitated, and the solution reservoirs were refilled with concentrated salt solutions, the iron sulfide–containing membranes still generated a membrane potential of a few tens to a hundred millivolts. Consistent with previous studies, this membrane potential was dependent on the concentrations of salts on either side of the membrane and is likely due to the adsorption of cations and/or anions on the charged inorganic membrane surfaces. In galvanostatic experiments in which current was applied across a precipitated iron sulfide membrane, the I/V characteristic curves of these Fe/S
membranes showed that the electrical resistance across the membrane changed at an inflection point (Fig. 7), indicating that the Fe-S precipitate membranes formed in these out-of-equilibrium systems are somewhat bipolar, that is, partially cation- and anion-selective. This is an important property of biological and also electrodialysis membranes (Honig and Hengst, 1970; Sakashita et al., 1983; Bauer et al., 1988; Strathmann et al., 1993; Aritomi et al., 1996).

The ability of simulated prebiotic iron sulfide chimney precipitates to facilitate electron transfer to a simulated Hadean ocean, with applied potentials between ±1 volt (relative to Ag/AgCl), is shown in Fig. 8. The simulated hydrothermal FeS membrane catalyst (grown on dialysis template then attached to a GCE) on the electrode facilitated ~0.4–0.8 mA of both anodic and cathodic current. No significant current (> tens of microamps) was observed with just the GCE, GCE with carbon tape, or in the ocean simulant containing FeS particles. Similar results, though at higher current ranging to ±10 mA, were observed when carbon cloth containing Fe/S precipitate was directly used as an electrode. As in the dialysis tubing experiments, the carbon cloth without Fe/S did not facilitate significant current at these potentials. The higher current range of Fe/S membranes on carbon cloth, compared to Fe/S membrane material taken from dialysis tubing, is likely due to the fact that the active surface area is greater on the carbon cloth working electrodes.

5.2. PEMFC function using geological electrocatalyst materials derived from iron meteorites

Electrochemical analyses of the PEMFC in operational mode revealed a stable open circuit voltage difference across the electrodes peaking close to 0.7 V (Fig. 9, upper panel). In the presence of Toluca electrocatalyst-impregnated GDLs, the current-voltage polarization curves (Fig. 9, lower panel) show distinct behavior confirming that the fuel cell is functional; and the current flow increases with decreasing voltage as expected, approaching a load of ca. 13 mA. In the absence of the geological catalyst components, no such polarization behavior was observed.

6. Discussion

The iron sulfide membranes that formed at the interface of contrasting solutions in our experiments represent specific mineral components that could have been contained within larger, carbonate- and silica-containing hydrothermal chimney precipitates on early Earth. Iron sulfide precipitates in a hydrothermal chimney, formed in pH/ion gradients via diffusion and self-assembly, could contribute to the electrocatalytic properties of the chimney if they were sufficiently conductive. Mackinawite (FeS) is usually the first
metastable product that forms from the precipitation of aqueous Fe$^{2+}$ and HS$^-$, and over time it can transform to greigite (Fe$_3$S$_4$), pyrrhotite, or pyrite (Kwon et al., 2011; Csákerényi-Malasics et al., 2012; Sines et al., 2012). Mackinawite is a layered mineral composed of Fe-S tetrahedra stabilized by van der Waals forces, and since the Fe-Fe distance is only 2.60 Å (similar to elemental n-iron: 2.48 Å), it is highly electrically conductive and has even been shown to exhibit superconducting characteristics (Kwon et al., 2011). It has been demonstrated that black smoker chimney material, which is also mostly composed of metal sulfides, is capable of converting the geochemical redox potential between hydrothermal fluid and seawater to electrical current and catalyzing redox reactions (Nakamura et al., 2010b). Even though a hydrothermal chimney at an alkaline vent on early Earth may not have had such a high fraction of metal sulfides as a modern black smoker chimney, still it is possible that in a prebiotic system subject to electrical potential gradients between hydrothermal fuels (e.g., H$_2$, CH$_4$) and seawater oxidants (e.g., CO$_2$, NO$_3^-$, NO$_2^-$, Fe$^{III}$), deposits of conductive Fe/S precipitates, aided by their large active surface area as seen in Fig. 6, might have been able to facilitate electron conduction and catalyze redox reactions on the mineral surfaces.

Our preliminary experiments revealed that, due to their far-from-equilibrium nature, inorganic precipitate membranes analogous to hydrothermal chimney walls have many unusual properties (van Oss, 1984) that may be biologically and/or prebiotically relevant. The growth of a hydrothermal chimney precipitate that separates contrasting solutions could generate and maintain an electrical potential for long periods of time yet still facilitate selective ion transfer through the membrane. The precipitates formed would likely exhibit a compositional gradient from exterior to interior, as is observed in real hydrothermal chimneys and chemical garden lab experiments (Haymon, 1983; Cartwright et al., 2002; Barge et al., 2012), and the charged mineral surfaces could adsorb and concentrate ions from either ocean or hydrothermal solution. Metal sulfide-containing chimneys formed within a temperature/pH gradient could potentially host a range of mineral phases with various electrochemical properties. It is likely that these inorganic membranes could also incorporate silicates, phosphates, Ni, and Mo into the precipitate (Barge et al., 2014; Barge and Kanik, unpublished data). More experimental work is needed to fully characterize the properties of geological mineral precipitates in far-from-equilibrium systems in order to understand the reactions that may be possible in hydrothermal chimney environments.

In some ways, the inorganic Fe/S precipitates that formed on carbon cloth in these interface experiments are similar to the ion-exchange membranes and gas diffusion layers in commercial as well as experimental fuel cells (Kim et al., 2009; Paulo and Tavares, 2011). The successful use of commercially available fuel cell electrode/GDL material (carbon cloth) as a template to precipitate simulated hydrogeological mineral catalysts is promising, as these fabricated electrodes can be directly used in PEMFC assemblies to catalyze redox reactions in a pressurized out-of-equilibrium geology test-bed reactor. Our preliminary PEMFC tests showed that geological minerals applied to the GDLs as catalysts have the potential to facilitate current flow and possibly catalyze redox reactions in putative geological fuel cells. Our methods proved successful for
FIG. 9. Open circuit voltage (upper panel) and polariza-

tion (I/V) curves of the Toluca MEA fuel cell (lower

panel). The negative sign in the I/V graph indicates that the

current is being taken from the functional fuel cell.

creating PEMFC MEAs with geological materials (Toluca

meteorite taenite and kamacite material) as electrode cata-

lysts and should work for any field sample or synthetic

material of similar composition.

Combined, these electrochemical techniques and fuel cell

reactor designs may allow for testing of specific reactions

that are proposed to be relevant to the emergence of me-

tabolism. For example, some metal sulfide minerals that

form under hydrothermal conditions are structurally similar

to the inorganic active centers of certain fundamental redox

enzymes (Russell and Hall, 1997; Rothery et al., 2008;

Baradaran et al., 2013; Nitschke et al., 2013), so synthetic

hydrothermal precipitates formed in the laboratory could be

evaluated as “proto-metalloenzymes” in electrochemical

and fuel cell studies. Experimentally testing the effects of

trace chemical components on the electron transfer capa-

bilities of a hydrothermal chimney could also be instruc-

tive. To give one example of this, Nitschke and Russell

(2013) proposed a denitrifying methanotrophic acetogenic

pathway for the origin of metabolism, where the energy

barriers from CH₄ to methanol and CO₂ to CO could be

solved through electron bifurcation by hydrothermally

produced Mo precipitating in trace amounts within a

chimney wall (Nitschke and Russell, 2009, 2011; Helz

et al., 2011). This is an interesting proposition, since, in

biology, energy barriers are also surmounted through elec-

tron shuttles such as quinones, flavins, and molybdenum

tungsten pterins (Darrouzet and Daldal, 2002; Staniek

et al., 2002; Herrmann et al., 2008; Li et al., 2008; Nitschke

and Russell, 2009, 2011, 2013; Kaster et al., 2011; Buckel

and Thauer, 2012; Poehlein et al., 2012; Schuchmann and

Müller, 2012). The end result of a fuel cell experiment

simulating a geoelectrochemical system would be to reveal

redox reactions in either half-cell as a function of the

composition of electrodes and membrane. In a simulation of

a prebiotic alkaline hydrothermal vent, for example, elec-

trical current could be produced by oxidation of hydro-

thermal H₂ to electrons and protons, thus driving the

reduction of oceanic CO₂ to formate and possibly further to

formaldehyde. Alternatively, hydrothermal CH₄ could be

oxidized to methanol and formaldehyde perhaps by using

nitrate or nitrite as an electron acceptor (Ducluzeau et al.,

2009; Nitschke and Russell, 2013; Russell et al., 2013).

Organic redox cofactors such as quinones, flavins, NADP,

FAD, GMP, and AMP that participate in electron transfer in

modern bioenergetics and were likely present in LUCA

(Buckel and Thauer, 2012; Schoepp-Cothenet et al., 2013)
could also be incorporated into fuel cell electrodes for

origin-of-life simulations.

Regardless of the specific parameters, approaching origin-
of-life experiments within a fuel cell/electrochemical frame-

work could allow experimenters to take advantage of the

many rigorous analytical methods and diagnostics that are

routinely employed in fuel cell tests. Moreover, there are

various computational models that can be used to model fuel

cell systems, none of which (to the best of our knowledge)
have been employed with an abiogenesis perspective in

mind. There are many reactions of importance to the origin

of life aside from the proto-metabolic redox reactions dis-

cussed above, such as RNA synthesis, formation of peptides

or other complex organics, and polymerization of phos-

phates to create energy currency. Any of these could be

incorporated into a fuel cell–like experiment and could

benefit from electrochemical techniques. For example, it has

been recently shown that Fe²⁺ can cause some biological

RNAs to become redox active (Athavale et al., 2012; Hsiao

et al., 2013). In an early Earth hydrothermal system, it is

possible that these redox-active RNAs might participate in

the electrocatalytic function of a hydrothermal chimney

system along with the inorganic components (cf. McGlynn

et al., 2012). Another example could be studying the gen-

eration of condensed and/or activated phosphates, which

are necessary at the origin of life to function as energy cur-

rency molecules similar to ATP (Baltscheffsky, 1996). It has

been proposed that green rust, a redox-active iron oxyhy-

droxide mineral that efficiently absorbs phosphate (Antony

et al., 2008; Barthélémy et al., 2012), might be capable of

forming pyrophosphate bonds via regulation of proton flow

through mineral layers (Arrhenius, 2003; Russell et al.,

2013); alternately, pyrophosphate could be formed via sub-

strate phosphorylation within a hydrothermally precipitated

membrane (Martin and Russell, 2007; Barge et al., 2014).
Incorporating components such as these into electrodes in a fuel cell experiment might yield new prebiotically plausible ways to synthesize necessary high-energy molecules.

7. Conclusions

There are many proven engineering design techniques and analytical methods for building membrane fuel cells and characterizing the electrochemical properties of different organic and inorganic catalysts. These techniques and methods can offer much insight into the workings of bioenergetics and metabolism if applied to biological and geological early Earth catalysis. Considering that (1) microbes and mitochondria may be viewed as highly evolved biological fuel cells and (2) that the earliest life on Earth was likely chemiosmotic, chemosynthetic, and utilized energy sources such as those commonly found in modern alkaline hydrothermal vents, we believe that the PFC modeling approach has potential. We argue that the electrochemical methods that have been successful in the fields of fuel cell development and bioelectrochemistry should be applied to simulating the origin of life because of the conspicuous fuel cell–like properties of metabolic and geo-electrochemical systems. The preliminary experiments presented here were successful in forming putative electrocatalytic minerals in out-of-equilibrium chemical systems, mimicking the formation of metal sulfide precipitates at the interface between ocean and hydrothermal fluids on early Earth. These inorganic membranes that simulate prebiotic submarine hydrothermal precipitates are shown to be structurally complex, capable of generating and maintaining membrane potentials and pH gradients, and electrically conductive. We also successfully formed simulated hydrothermal chimney precipitates on commercial fuel cell electrode/GDL material, a technique that can be used to create electrode components for various types of fuel cell experiments. Finally, we developed a PEMFC for simulating geo-electrochemical processes and demonstrated that the PEMFC is operational when field samples of geological material are used as the electrode catalysts. The methods used in this work are easily generalized to other geochemical interfaces of interest, such as water-rock reactions on early Mars or the icy moons. Moving toward this type of laboratory simulation of the emergence of bioenergetics will not only be informative in the context of the origin of life on Earth but may help in understanding whether it is possible for life to have emerged in similar environments on other planets.

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Author Disclosure Statement

No competing interests exist.

Abbreviations

ATP, adenosine triphosphate; GCE, glassy carbon electrode; GDLs, gas diffusion layers; LUCA, last universal common ancestor; MEA, membrane electrode assembly; MFCs, microbial fuel cells; PEM, proton exchange membrane; PEMFC, proton exchange membrane fuel cell; PFC, prebiotic fuel cell.

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