
High-Temperature Alkaline Water Electrolysis

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Overall Objectives

The overall objective is to develop high-temperature alkaline water electrolysis using molten hydroxides impregnated in porous alumina, zirconia, or lithium aluminate. It is described in more detail below:

- Develop alumina- and zirconia-based matrices with good corrosion resistance.
- Develop anode and cathode catalysts with enhanced hydrogen evolution reaction and oxygen evolution reaction activity.
- Assemble single electrolyzer cells and test their performance and durability (at 0.5–1.0 A/cm²).
- Perform economic analysis of high-temperature alkaline water electrolysis in terms of materials cost and system efficiency (high heating value).

Fiscal Year (FY) 2019 Objectives

- Identify/select metal oxides stable in molten hydroxide electrolytes.

- Optimize the corrosion resistance of non-active cell components in molten hydroxide electrolytes.
- Demonstrate single cell performance of <1.5 V at 1,000 mA/cm² at temperature 450°C to 550°C.
- Evaluate energy balance and compression cost of a 1 MW electrolyzer stack system.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan¹:

- (A) Operating cost: prohibitive electricity consumption for water electrolysis
- (B) Capital cost: associated with platinum group metal or expensive high-temperature materials

Technical Targets

This project will develop high-temperature alkaline water electrolysis to meet the detailed targets below and in Table 1:

- Composite electrolyte OH⁻ conductivity >0.1 S/cm at 350°C to 550°C.
- Per-cell area specific resistance (ASR) of ≤0.2 Ohm-cm² at 350°C to 550°C using a membrane thickness of 200 μm.
- Single cell performance <1.5 V at 1,000 mA/cm² at temperature <550°C.
- Stack electrical efficiency >90% low heating value (LHV) hydrogen with current density at 1.0 A/cm².

FY 2019 Accomplishments

- Identified matrix material stable at 550°C under simulated electrolyzer operating conditions. Li₂ZrO₃ matrix material showed long-term stability in molten hydroxide electrolyte after testing for 500 h.

¹ <https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22>

- Evaluated the corrosion mechanism of stainless steel alloys (310 and 316) and Ni-200 sheets with and without molten Li/Na hydroxide under oxidizing and reducing atmosphere at 600°C.
- Demonstrated high-temperature alkaline water electrolysis cell performance and durability using different matrix thicknesses, and successfully achieved cell performance of 1.5 V at a current density of 1,000 mA/cm² at 550°C and durability over the period of 120 h.
- Successfully conducted cost analysis compared to the polymer electrolyte membrane (PEM)-based electrolyzer system, and performed energy balance of a 1 MW plant.

Table 1. Distributed Forecourt Water Electrolysis Hydrogen Production

Characteristic	Units	2011 Status	2015 Target	2020 Target
Hydrogen Levelized Cost (Production Only)	\$/kg H ₂	4.20	3.90	2.30
Electrolyzer System Capital Cost	\$/kg	0.70	0.50	0.50
	\$/kW	430	300	300
System Energy Efficiency	% (LHV)	74	76	77
	kWh/kg	45	44	43
Stack Energy Efficiency	% (LHV)	74	76	77
	kWh/kg	45	44	43
Electricity Price	\$/kWh	From AEO 2009	From AEO 2009	0.037

AEO – Annual Energy Outlook

INTRODUCTION

Hydrogen production for mobile and stationary energy storage applications from water electrolysis is attractive due to its high efficiency, fast ramp rates, and high-pressure capability. However, current hydrogen production from electrolysis comprises only a small fraction of the global hydrogen market due to the high cost associated with expensive stack materials (membrane, catalyst, and bipolar plates) and electricity consumption of the commercially available electrolysis systems. This project aims to develop a high-temperature alkaline water electrolyzer that can simultaneously reduce the electrolyzer cost (by adopting cheaper materials) and improve energy efficiency (due to enabling high-temperature operation). The project will use high-temperature alkaline electrolysis that employs single or binary hydroxide (lithium, sodium, or potassium hydroxide) impregnated into a porous oxide matrix as the electrolyte membrane.

The operating temperature of alkaline water electrolysis can vary from 350°C to 550°C depending on the category and ratio of each individual electrolyte. In this process, single or mixed alkali/alkaline earth hydroxides (LiOH, NaOH, KOH, Ca(OH)₂, etc.) will be first melted and then impregnated into a porous matrix of alumina or zirconia. The meticulously designed alumina or zirconia matrices can effectively retain molten hydroxides via capillary forces [1–3]. The alumina or zirconia containing single or mixed hydroxides will be used as the electrolyte for alkaline electrolysis that can operate over a wide range of temperatures that is tunable by the choice of single or eutectic system employed. Ni or Co catalysts will be used for the anode and cathode reactions, respectively. A key factor that will influence the success of this technology is the microstructures of the porous oxide matrices. Their thickness, porosity, and pore structure largely determine whether they can successfully retain molten hydroxides within their pores, particularly over an extended period of time (DOE target 7 years).

APPROACH

The approaches to achieve the technical targets are listed in Table 2. The technical targets will be validated first in a single electrolyzer cell and then an energy balance will be performed for a 1 MW electrolyzer stack.

Table 2. Approaches to Achieve High-Temperature Alkaline Water Electrolysis

Technical Targets	Approaches
Stability of metal oxide materials in molten hydroxide melts	Explore/select stable metal oxide in molten hydroxide electrolyte under electrolysis conditions
Develop corrosion mechanism of non-active cell components	Optimize corrosion of current collector in molten hydroxide electrolyte
Single cell performance <1.5 V at 1,000 mA/cm ² at temperature 450 °C to 550 °C	Adopt robust electrolyte matrix Employ high-performance catalysts Mitigate hot corrosion-caused component resistance increase
Perform energy balance for 1 MW electrolyzer stack	Conduct compression cost based on 1 A/cm ² active area and operating current density Perform energy balance at 450 °C, 1.50 V/cell and 550 °C, 1.40V/cell

RESULTS

The electrolyte matrix provides ionic transport, gas separation, and perimeter seal formation. It is a densely packed powder bed impregnated with an alkali electrolyte to form a composite paste-like structure at the operating temperature (250°–550°C). For the electrolyzer matrix, good mechanical and chemical stability are desired to prevent crack propagation due to thermal and mechanical stresses during the heat treatment and operation of the electrolyzer cell.

Selected matrix materials (e.g., LiAlO₂, SiC, YSZ, and Li₂ZrO₃) were immersed separately in mixtures of LiNa hydroxide electrolyte. The matrix materials and molten LiNa hydroxides were put in a platinum crucible and placed within a sealed alumina reactor. The alumina reactor was subsequently heated to 550°C at 3°C/min. The immersion test was conducted at 550°C under 3% H₂O-N₂ atmosphere for 50 h. The long-term immersion test of the Li₂ZrO₃ matrix was conducted at 550°C under 3% H₂O-N₂ atmosphere for 500 h. After the completion of the experiments, the matrix material was washed with distilled water to dissolve the hydroxides. Subsequently, the powder was dried at 80°C for characterization. Morphological and elemental analyses were performed using an FEI Quanta 250 FEG scanning electron microscope (SEM) attached to an energy dispersive X-ray spectroscopy. A Bruker AXS D-8 Advance X-ray diffractometer (XRD) was used for the identification of phases present in test samples.

First, we investigated the influence of molten Li/Na hydroxides at 550°C on the phase stabilities of the as-received selected matrix powders for short-term testing (50 h) and long-term testing (500 h). Figure 1 displays XRD patterns of the as-received selected matrix materials (LiAlO₂, SiC, YSZ, and Li₂ZrO₃) and samples obtained after the immersion test in molten Li/Na hydroxides at 550°C under 3% H₂O-N₂ atmosphere for 50 h and 500 h. After the immersion test, we observed the crystalline phase of β-LiAlO₂, indicating that the α-LiAlO₂ phase transformation to the β-LiAlO₂ phase occurred in molten hydroxide at 550°C under 3% H₂O-N₂ atmosphere (Figure 1a). Notably, the diffraction peaks of the α-phase narrowed and their intensity decreased greatly after an immersion time of 50 h. We found that the SiC material was unstable in molten Li/Na hydroxide during the 50 h immersion test (Figure 1b). The crystalline phase of SiC transformed into the Li₂SiO₃ phase, followed by growth of a new phase. This result indicates that the SiC actively reacted with alkaline hydroxide to form a new crystal with particle coarsening. We also found that the as-received YSZ material transformed into the Li₂ZrO₃ monoclinic phase after the 50 h immersion test (Figure 1c). Thus, we concluded that YSZ undergoes chemical reaction with molten Li/Na hydroxides under 3% H₂O-N₂ atmosphere. We observed no evidence for the formation of other phases in the molten Li/Na hydroxide under 3% H₂O-N₂ atmosphere after the 500 h immersion test (Figure 1d). Thus, we conclude that Li₂ZrO₃ undergoes no chemical reaction with molten Li/Na or Na/Cs hydroxide melts and no structural change. Indeed, Li₂ZrO₃ remained in its original monoclinic phase with no substantial change in weight after immersion for over 500 h.

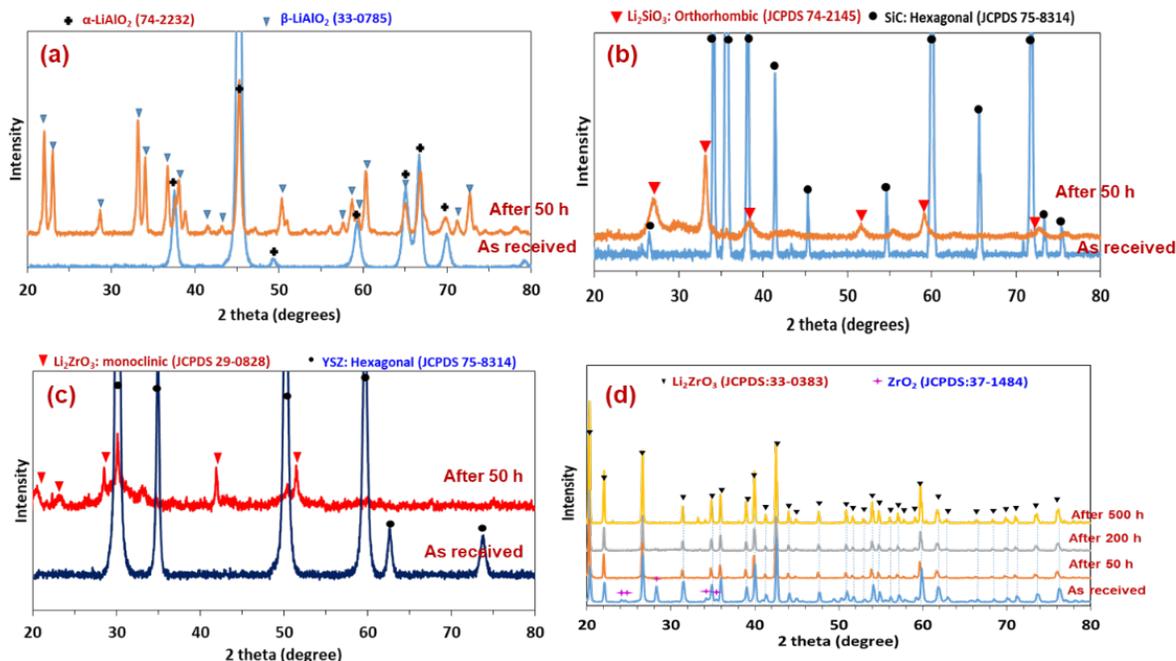


Figure 1. XRD patterns of the (a) LiAlO₂, (b) SiC, (c) YSZ phase stability in molten Li/Na hydroxides at 550 °C under 3% H₂O-N₂ atmosphere for 50 h, and (d) Li₂ZrO₃ long-term stability for 500 h.

To evaluate corrosion of inactive components, eutectic Li-Na hydroxide melt was applied on the surface of as-received nickel and stainless-steel samples. Coated samples were placed within a sealed horizontal alumina tubular reactor. The alumina reactor was subsequently heated to 600°C at 3°C/min. The immersion test was conducted at 600°C under controlled atmosphere comprising oxidizing (3% H₂O-air) and reducing (4% H₂-3% H₂O-N₂ balance) atmospheres for 50 h. After the completion of the experiments, the metal alloys were washed with distilled water to dissolve the hydroxide. The metal alloys were dried at 80°C and stored in a dry sample container for further characterization. A similar test setup and procedure were used for conducting corrosion tests on metal coupons in the absence of electrolyte. All the post-test samples were analyzed to identify the nature of the oxide scales formed in the presence of Li/NaOH under the oxidizing condition.

Figure 2a shows stainless steel (SS) and Ni samples after 50 h exposure to 3% H₂O-air at 600°C in absence of Li/NaOH. SS (310 and 316) and Ni samples all showed the formation of a uniform protective oxide layer on the surface. The samples in the presence of Li/NaOH under 3% H₂O-air faced severe corrosion, which led to a distinct oxide scale formation on the metal surface (Figure 2b) as compared to the oxide layer that formed in the absence of Li/NaOH. Formation of porous scale on the surface of each sample was observed after 50 h. As compared to SS samples (Figure 2a [b and e]), the oxide scales formed on Ni are observed to be more porous (Figure 2b [h]) after 50 h. After 200 h, the porosity in the oxide scale increased for both the SS samples (Figure 2b [c and f]) and Ni (Figure 2b [i]).

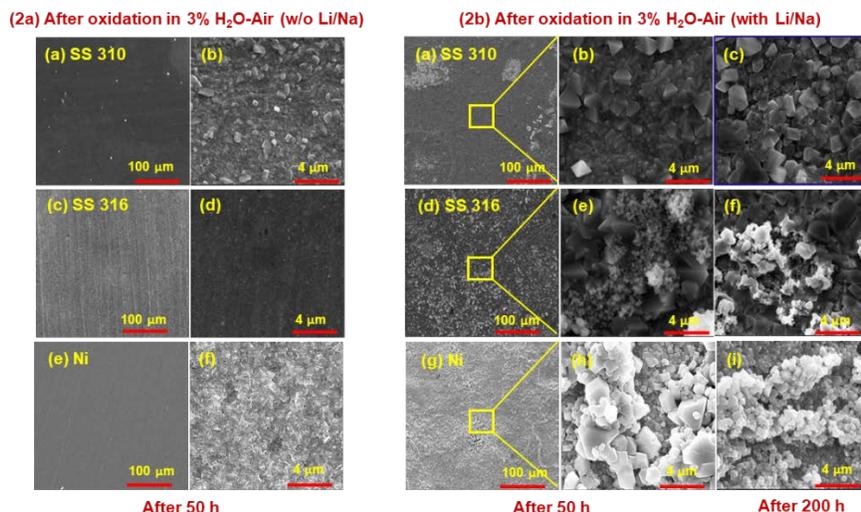


Figure 2. (a) SEM micrographs show polished surface and oxidized at 600 °C for 50 h under 3% H₂O-air for SS310 [a–b], SS316 [c–d], and Ni [e–f]. (b) SEM micrographs of SS310 for 50 h [a–b] and 200 h [c], SS316 for 50 h [d–e] and 200 h [f], and Ni for 50 h [g–h] and 200 h [i], exposed to 600 °C in 3% H₂O-air with molten Li/Na hydroxide.

The electrolyzer button cell (13 cm²) was designed and evaluated. We explored the effect of various thicknesses of matrices on the electrolyzer cell performance and durability at different temperatures (e.g., 450 °C to 550 °C). In this cell, N₂ gas humidified at 90 °C was introduced into the cathode cell frame to initiate the water electrolysis. Figure 3a shows the polarization curve of the electrolyzer cell operated at different temperatures with matrix thickness of 450 μm. The electrolyzer cell voltages were 1.50 V at 550 °C, 1.80 V at 500 °C, and 1.87 V at 450 °C, respectively, for a constant current density of 1,000 mA/cm². The increase of temperature from 450 °C to 550 °C significantly increased the cell performance (almost 0.37 V), probably due to the increased rates of the electrochemical reactions. Furthermore, the increase of temperature leads to improved ionic conductivity of the electrolyte that could also have an impact on the operation of the electrolyzer cell. We also performed long-term cell durability testing at different temperatures. The electrolyzer cell under a constant current density at 1,000 mA/cm² exhibits a very stable performance at 550 °C (Figure 3b). The cell durability test shows no obvious degradation when the cell operated for ~120 h. In order to determine the cell durability at different temperatures, the cell performance at 500 °C and 450 °C was also tested at constant current density of 1,000 mA/cm² after cell temperature decreased, again, the cell voltage increased following the temperature decrease. However, the cell voltage immediately recovered to 1.50 V after the cell temperature was increased to 550 °C. These results demonstrated that the electrolyzer cell had a good durability upon temperature swing.

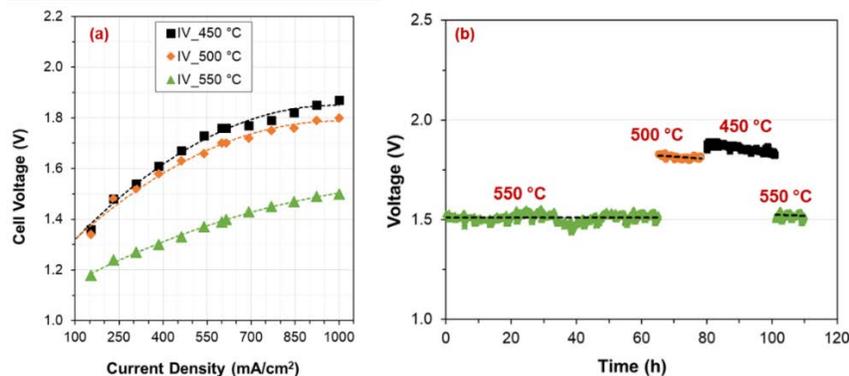


Figure 3. Polarization curve of high-temperature alkaline water electrolysis electrolyzer cell (13 cm²) at different temperatures (450 °–550 °C) using matrix thickness of 450 μm: (a) cell performance and (b) cell durability ~120 h.

We conducted an energy balance case study for a 1 MW plant operating at 1.4 V, 1,000 mA/cm², assuming 90% heat recovery from the electrolysis system (as shown in Figure 4a). Operating the cell above thermal neutral voltage (VTn) (1.28 V at 550°C) results in excess heat from the system (an inefficiency that can be used to heat the system). Operating below or near VTn can require a significant amount of energy to heat the system (trim heater). For this system the efficiency is 91.4% using high heating value, showing a loss of 150 kW (i.e. required cooling). The energy equations take into account latent heat (Hv) and water losses from gas exhaust streams (additional water feed required to maintain balance). The cost analysis shown in Figure 4b is based on performance of 1.40 V at 1,000 mA/cm² with an efficiency of 39.3 kWh/kg H₂. The calculated total hydrogen production cost is \$5.05/kg H₂, far below \$6.44/Kg H₂ using PEM water electrolysis. It is expected that this cost can be further reduced as we continue improving cell performance.

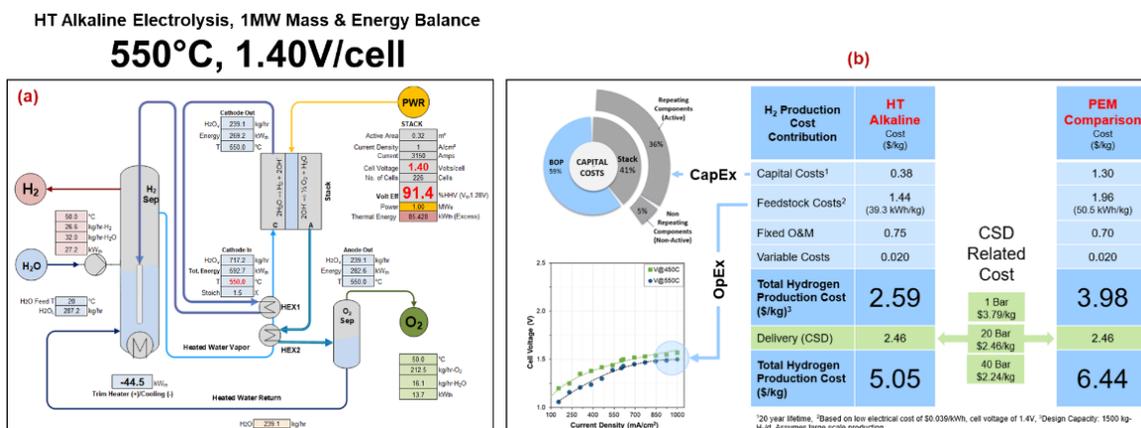


Figure 4. (a) Energy balance and (b) cost analysis of 1 MW high-temperature alkaline water electrolysis

CONCLUSIONS AND UPCOMING ACTIVITIES

First, we have studied the stability of a series of matrix and current collector materials exposed to conditions mimicking high-temperature alkaline water electrolysis operations. These studies provide insights into building these components with long lifetimes.

- The LiAlO₂, SiC, and YSZ are unstable in molten Li/Na hydroxides at 550°C under 3% H₂O-N₂ atmosphere for 50 h.
- Li₂ZrO₃ material showed phase and microstructure stability upon exposure to molten Li/Na hydroxide at 550°C for 500 h.
- Both stainless steel alloys (310 and 316) and Ni-200 sheets formed porous oxide scales on their surfaces after being exposed to molten hydroxides.

Second, we have demonstrated high-temperature alkaline water electrolysis cell performance and durability using different matrix thicknesses. We successfully achieved cell performance of 1.5 V at a current density of 1,000 mA/cm² at 550°C and durability over the period of 120 h.

Finally, we conducted the energy balance case study for a 1 MW plant assuming 90% heat recovery from the high-temperature electrolysis system. The calculated total hydrogen production cost is \$5.1/kg H₂ (high-temperature alkaline water electrolysis), far below \$6.4/kg H₂ from PEM water electrolysis.

In the future, we will obtain better high-temperature alkaline water electrolysis cell performance and durability with a more durable matrix; we can realize this by employing the new Li₂ZrO₃ matrix that is stable under molten hydroxide medium. We will also resolve corrosion of current collectors. This will be done using alternative materials to Ni and SS or adding a protective layer on the surface of Ni and SS.

SPECIAL RECOGNITIONS AND AWARDS/PATENTS ISSUED

1. Hui Xu and Kailash Patil, “Components for High-Temperature Alkaline Water Electrolysis,” US Patent filed (2019).

FY 2019 PUBLICATIONS/PRESENTATIONS

1. Kailash Patil, Judith Lattimer, Steve McCatty, and Hui Xu, “High-Temperature Alkaline Electrolyte for Energy Conversion,” 236th ECS meeting (invited), abstract submitted, October 2019.
2. Kailash Patil, Andrew Sweet, Steve McCatty, Winfield Greene, and Hui Xu, “Components Improvement for High-Temperature Molten Alkaline Water Electrolysis,” 235th ECS meeting, abstract submitted, May 2019.

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3. K. Patil, S.P. Yoon, J. Han, S.W. Nam, T.H. Lim, and I.H. Oh, “The Effect of Lithium Addition on Aluminum Reinforced LiAlO₂ Matrix for Molten Carbonate Fuel Cells,” *International Journal of Hydrogen Energy* 36 (2011): 6237–6247.