
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 in porous-based alumina, zirconia, or lithium aluminate. Some of our targets are below.

- Develop alumina- and zirconia-based matrices with good corrosion resistance.
- Develop anode and cathode catalysts with enhanced hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) activity.
- Assemble and test single electrolyzer cells and test their performance and durability (at 0.5–1.0 A/cm² and 1,000 hours).
- Construct and test a 1.8-kW electrolyzer stack.

Fiscal Year (FY) 2018 Objectives

- Develop alumina- and zirconia-based matrices.
- Measure the OH⁻ ion conductivity of the composite electrolyte.
- Optimize slurry formulation of the catalysts using the tape casting process.

- Demonstrate single cell performance <1.5 V at 1,000 mA/cm² at temperature <550°C.

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 metals or expensive high-temperature materials.

Technical Targets

This project will develop high-temperature alkaline water electrolysis.

- Composite electrolyte OH⁻ conductivity >0.1 S/cm in temperature of 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% lower heating value (LHV) hydrogen with current density at 1.2 A/cm².

FY 2018 Accomplishments

- Achieved composite electrolyte OH⁻ conductivity >0.1 S/cm while the temperature ranged from 350°C to 550°C.
- Obtained per-cell ASR of ≤0.2 Ohm-cm² using a membrane thickness of 100–200 μm.
- Successfully developed strategies to mitigate hot corrosion of high-temperature alkaline electrolysis (HTAE) components including current collectors and end plates.

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

- Successfully demonstrated single cell performance <1.5 V at 1,000 mA/cm² at temperature <550°C.

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 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 program aims to develop a high-temperature alkaline water electrolyzer that can simultaneously reduce the electrolyzer cost (by adopting low-cost material) and improve energy efficiency (due to enabling high-temperature operation). The project will use HTAE 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 HTAE can vary from 350°C to 550°C, dependent on the category and ratio of each individual electrolyte. In this process, single or mixed alkali/alkaline earth hydroxides (LiOH, NaOH, or KOH) can be first melted and subsequently impregnated in three porous metal oxides—MO-1, MO-2, or MO-3. The meticulously designed metal oxide matrices can well retain molten hydroxides via capillary forces [1–2].

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 in 1.8-kW electrolyzer stack tests.

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

Technical Targets	Approaches
Composite electrolyte OH ⁻ conductivity >0.1 S/cm in temperature of 350 °C to 550 °C	Explore different composite electrolytes to increase the OH ⁻ conductivity
Per-cell ASR of membranes ≤0.2 Ohm-cm ² at 350 °C to 550 °C	Develop thin alumina- or zirconia-based matrices with good mechanical strength Adopt electrolyte with high OH ⁻ conductivity
Single cell performance <1.5 V at 1,000 mA/cm ² at temperature 300 °C to 550 °C	Adopt membranes with low ASR Employ high-performance catalysts Mitigate hot-corrosion-caused component resistance increase

RESULTS

The matrix robustness (to withstand thermomechanical stress) impacts the electrolyzer’s performance and endurance. In this project, both aluminate- (MO-1) and zirconia (MO-3)-based matrix metal oxides were used as the matrix support materials. Thin aluminate- and zirconia-based matrices were fabricated using the tape casting method. The green tape fabrication of the electrolyte support matrix was optimized for a solvent based slurry formulation process. The temperatures for binder and pore-former removal and for subsequent sintering processes were determined using heating/cooling cycles. The heating rate for removing binder was 3°C/min up to 425°C and the cooling rate was 5°C/min down to room temperature. The microstructure and porosity/pore size of the sintered matrices were analyzed by scanning electron microscopy (SEM) and Hg-porosimetry (AutoPore IV, Micromeritics).

The fabrication of a green sheet tape using a doctor blade and green sheet matrix’s thickness is shown in Figure 1(a). A SEM image of sintered metal oxide matrix showed porous structure and no cracks were observed after sintering at 550°C in air atmosphere for 2 h (Figure 1(b)).

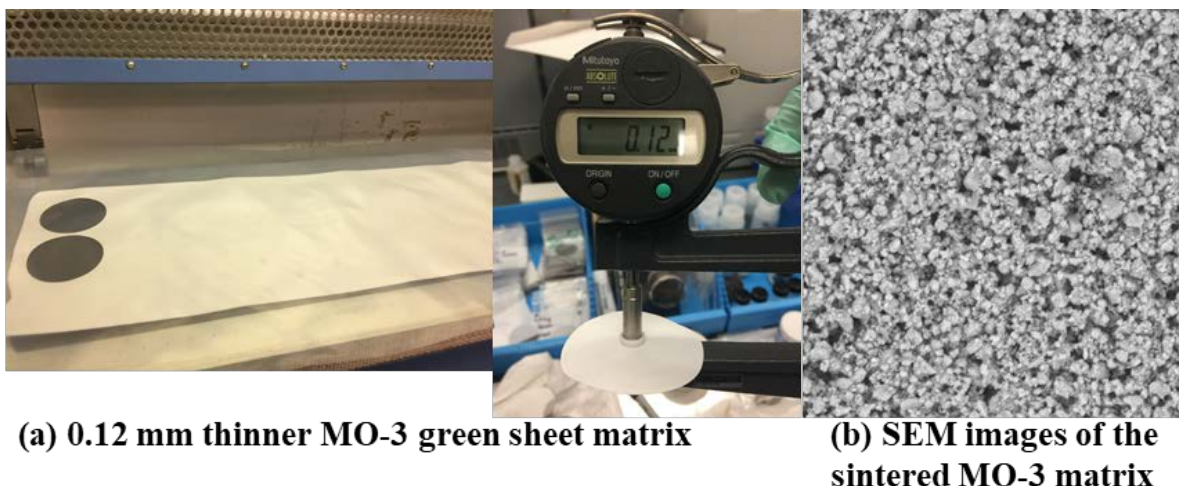


Figure 1. Fabricated metal oxide green sheet matrix: (a) 0.12 mm matrix thickness and (b) SEM image of MO-3 matrix sintered at 550°C for 2 h

The phase and microstructural changes of metal oxides in hydroxide medium were evaluated. We immersed metal oxides in molten ($\text{Li}_{0.52}/\text{Na}_{0.48}$)OH melts at 550°C for 10 h and 100 h time periods. The X-ray diffraction (XRD) patterns of MO-1 and MO-3 powders before and after their immersion tests are shown in Figure 2. The crystalline phase of $\gamma\text{-LiAlO}_2$ reveals that MO-1 phase transformation occurred in molten hydroxide for a 10 h duration (Figure 2, top panel); the minor phases of $\gamma\text{-LiAlO}_2$ and lithium aluminum hydroxide hydrate appeared after performing the immersion test for 10 h. Increasing the immersion time to 100 h caused the intensity of MO-1 peaks to increase. The XRD patterns of the MO-3 powders obtained after immersion in molten (Li/Na)OH at 550°C for different lengths of time are shown in the bottom panel of Figure 2. The MO-3 powder was more stable and no apparent reactions with molten Li/Na hydroxide melts were observed. The minor phase of lithium hydroxide hydroxyl hydrate ($\text{LiOH}(\text{OH})_2\cdot\text{H}_2\text{O}$) was not completely removed during the washing process after immersion test.

The OH^- ion conductivities of the single or binary mixture of the electrolyte samples were measured. The temperature dependence of OH^- conductivities for the hydroxide/metal oxide composites is shown in Figure 3(a). The binary LiOH/NaOH hydroxide melt demonstrated the highest OH^- ion conductivity, 0.52 S/cm at 550°C. The conductivity of the single/binary hydroxide electrolyte improved with increased temperature. The ASRs of the prepared matrices are shown in Figure 3(b). It is clearly seen that the ASR decreased as the temperature increased from 350°C to 550°C. The lowest ASR was only 0.02 Ohm-cm².

The green sheet electrodes with a variety of thicknesses (0.20 to 0.25 mm) were developed in the lab using doctor blade. The electrolyzer button cells (13 cm²) were tested to evaluate the HTAE performance. Button-cell components including anode and cathode frame and current collectors were made with high-corrosion-resistance stainless steel (S316) materials. The hydroxide electrolyte powders were stored in the cathode channel of the separator. During the cell conditioning process, the hydroxide electrolyte easily penetrated into the matrix from the cathode channels after the organic additives burned out.

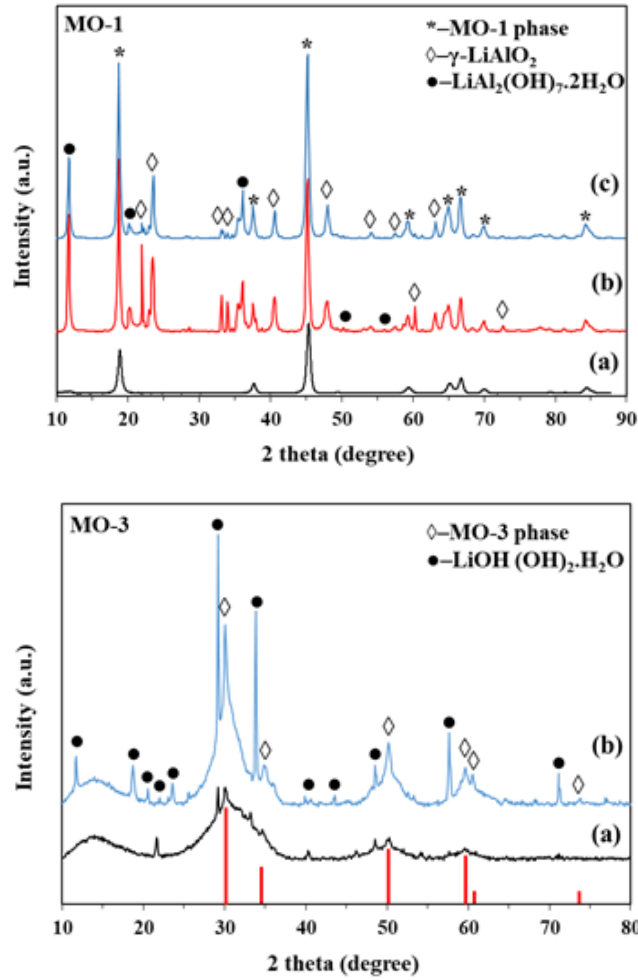


Figure 2. XRD patterns of metal oxide powder immersion in molten (Li/Na)OH at 550 °C. (Top) MO-1: (a) powder as received, (b) 10 h, and (c) 100 h duration. (Bottom) MO-3: (a) 10 h and (b) 100 h duration (red lines indicate the assigned of pure phase of MO-3 powder).

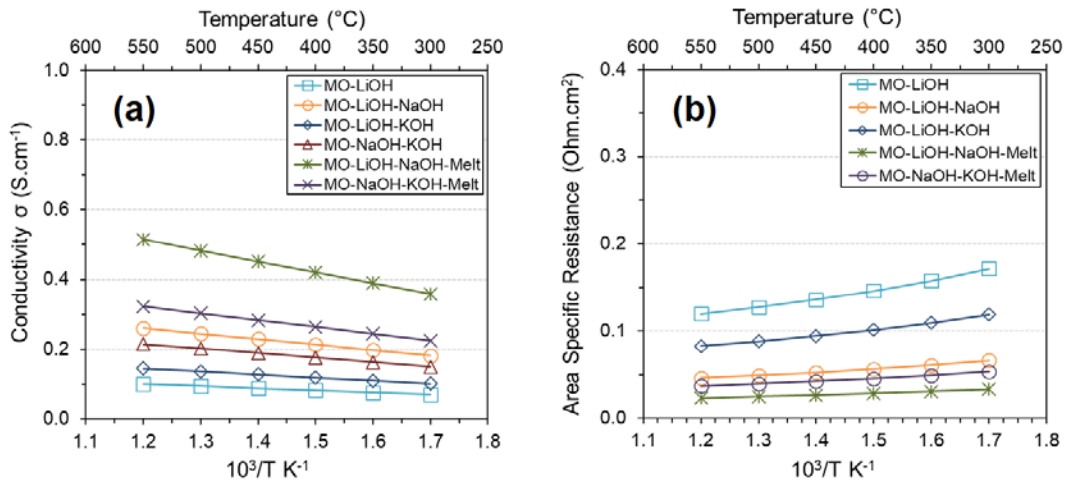


Figure 3. (a) Temperature dependence of the OH⁻ ion conductivity of single/binary hydroxides at 300°–550 °C in air atmosphere; (b) ASR at 300°–550 °C in air atmosphere and thickness of 0.12 mm

We have made tremendous progress in improving the cell performance by improving anode and cathode catalyst activity, adopting matrix with small thickness but good mechanical strength, reducing component corrosion, and optimizing operating conditions. As a result of corrosion reduction and thinner matrix, the high-frequency resistance dropped substantially, and the cell performance improved accordingly. A single cell performance of 1.5 V at 1,000 mA/cm² at 550°C was achieved as shown in Figure 4(a). The 30-hour durability at 600 mA/cm² was demonstrated in Figure 4(b) and the performance continued improving during the course of durability testing.

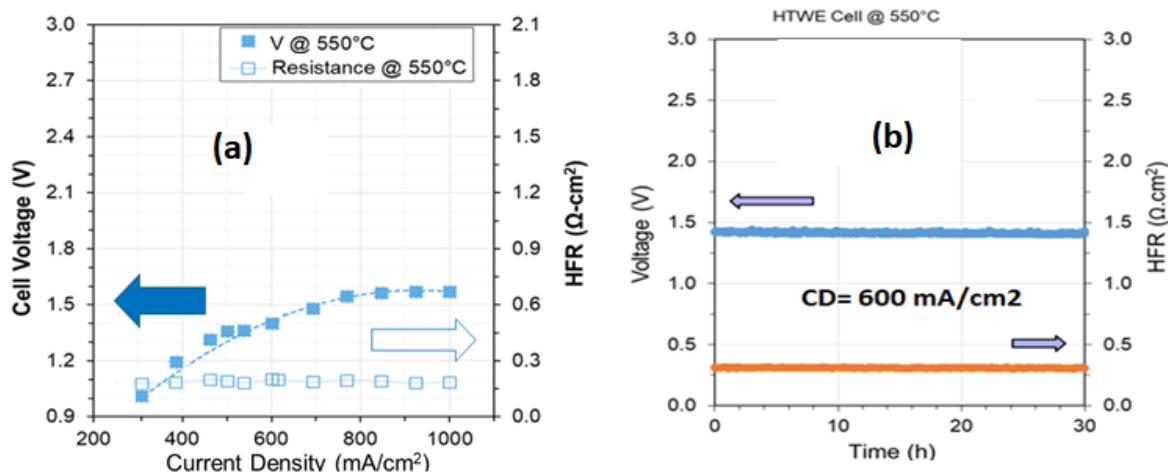


Figure 4. HTAE cell (13 cm²) performance and durability: (a) single cell performance; (b) durability test up to 30 hours

CONCLUSIONS AND UPCOMING ACTIVITIES

- Successfully developed metal oxide matrices in various materials and thickness using the tape casting process.
- Achieved superior OH⁻ ion conductivity and low ASR. High OH⁻ ion conductivity up to 0.5 S/cm of molten binary hydroxide was achieved.
- Successfully developed cathode and anode electrodes using the tape casting process.
- Designed and constructed high-performance HTAE cells. Successfully demonstrated single cell performance <1.5 V at 1,000 mA/cm².

We will strive to further improve the HTAE cell performance at lowered temperature (~450°C), reduce component corrosion, and design a 10-cell short stack that will meet targeted performance, durability, and energy efficiency.

- Evaluate the matrix solubility in hydroxide electrolyte from 400°C to 550°C.
- Further optimize component and operating conditions of the long-term single cell durability.
- Design the stack cell components to construct a 1.8-kW stack.

FY 2018 PUBLICATIONS/PRESENTATIONS

1. Hui Xu and Kailash Patil, "High Temperature Alkaline Water Electrolysis," presented at the 2018 DOE Annual Merit Review and Peer Evaluation Meeting, Washington, DC, June 2018.
2. Kailash Patil, Andrew Sweet, Winfield Greene and Hui Xu, "High-Temperature Molten Alkaline Water Electrolysis," 233rd ECS meeting, Seattle WA, May 2018.

3. Hui Xu and Kailash Patil, “Components for High-Temperature Alkaline Water Electrolysis,” provisional patent, filed in 2018.

REFERENCES

1. “H₂ Production and Delivery Cost Apportionment,” DOE Hydrogen and Fuel Cells Program Record #12001 (2012), http://www.hydrogen.energy.gov/pdfs/12001_h2_pd_cost_apportionment.pdf.
2. D. Anthony, J. Rand, and R. Dell, *Hydrogen Energy Challenges and Prospects* (RSC Energy Series, 2008), DOI:10.1039/9781847558022.