

II.B.4 High Temperature Alkaline Water Electrolysis

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(F) System Efficiency and Electricity Cost: associated with platinum group metals or expensive high temperature materials

(G) Operating cost: prohibitive electricity consumption for water electrolysis

Technical Targets

This project will develop high-temperature alkaline water electrolysis.

- Composite electrolyte OH⁻ conductivity >0.1 S/cm in temperature of 350–550°C
- Per cell area-specific resistance of ≤0.2 ohm-cm² at 350–550°C using a membrane thickness of 200 μm
- Stack electrical efficiency >90% lower heating value (LHV) H₂ with current density at 1.2 A/cm²

Overall Objectives

The overall objective is to develop high-temperature alkaline water electrolysis using molten hydroxides in porous alumina, zirconia, or lithium aluminate. Some of our objectives are below.

- Develop alumina- and zirconia-based matrices.
- Select anode and cathode catalysts with enhanced hydrogen evolution reaction and oxygen evolution reaction activity.
- Assemble and test 25-cm² single electrolyzer cell and evaluate its performance and durability (at 0.5–1.0 A/cm² and 1,000 h).
- Construct and test 1.8 kW electrolyzer stack.

Fiscal Year (FY) 2017 Objectives

- Develop alumina- and zirconia-based matrices with optimal pore size.
- Optimize slurry formulation of the alumina and zirconia matrices using tape casting process.
- Impregnate hydroxides into porous matrices to achieve target conductivity.

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 Plan and contributes to the achievement of the targets shown in in Table 1.

TABLE 1. Distributed Forecourt Water Electrolysis Hydrogen Production Targets

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

FY 2017 Accomplishments

- Selected stable metal oxide matrices via investigating the stability of different metal oxides in single and binary hydroxide melts.
- Successfully fabricated and optimized lab-scale alumina- and zirconia-based matrices using a tape casting process.
- Constructed a testing facility for OH⁻ conductivity measurement and matrix stability in molten hydroxide systems.



INTRODUCTION

Hydrogen production from water electrolysis for mobile and energy storage applications 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 cheap material) and improve energy efficiency (due to enabling high-temperature operation).

APPROACH

The proposed project uses high-temperature alkaline electrolysis that employs lithium, sodium, potassium, or calcium hydroxide impregnated into a porous oxide matrix as the electrolyte membrane as shown in Figure 1.

The operating temperature of modal acoustic emissions can vary from 350°C–550°C, dependent on the category and ratio of each individual electrolyte. In this process, single or mixed alkali/alkaline earth hydroxides (LiOH, NaOH, and KOH) are first melted and impregnated in porous matrix of alumina or zirconia. The meticulously designed alumina or zirconia matrices can well retain molten hydroxides via capillary forces [1,2]. The alumina or zirconia containing single or mixed hydroxides is used as the electrolyte for alkaline electrolysis that can operate very flexibly in a wide temperature range, dependent on single or eutectic system.

Ni- or Co-based catalysts will be used for the anode and cathode reactions.

A key factor that will influence the success of this technology is the microstructures of the porous oxide matrices. Their thickness, porosity, and pore structures largely determine whether they can successfully retain molten hydroxides in their pores, particularly over an extended period of time (DOE target, 7 years). Therefore, our overall approach is to develop the alumina- or zirconia-based matrices and design composite electrolytes with various hydroxides in order to increase the OH⁻ conductivity. Alumina- or zirconia-based matrices will be developed and slurry formulation and tape casting process be optimized to achieve thin composite electrolyte with good mechanical strength.

RESULTS

The short-term stability of baseline powder and advanced metal oxides in single and binary hydroxide electrolyte immersion was tested at 450°C and 550°C for 10 h under air atmosphere. Shown in Figure 2a are the surface morphologies of baseline metal oxide (α -Al₂O₃) powder after exposure to LiOH and LiOH-NaOH melts in air at 450°C and 550°C for 10 h. The as-received powder consists of uniform spherical micron-size particles. Heating this baseline powder at 450°C and 550°C in both LiOH and LiOH-NaOH melts resulted in the emergence of rod-shaped Al₂O₃ particles. Significant changes in morphology of the baseline metal oxide (MO) were observed after the immersion test. Figure 2b–d shows the surface morphologies of MO-1, 2, and 3 powders after exposure to the same LiOH and LiOH-NaOH melt conditions. The microstructures of MO-1, 2, and 3 powders reveal that the particles were well

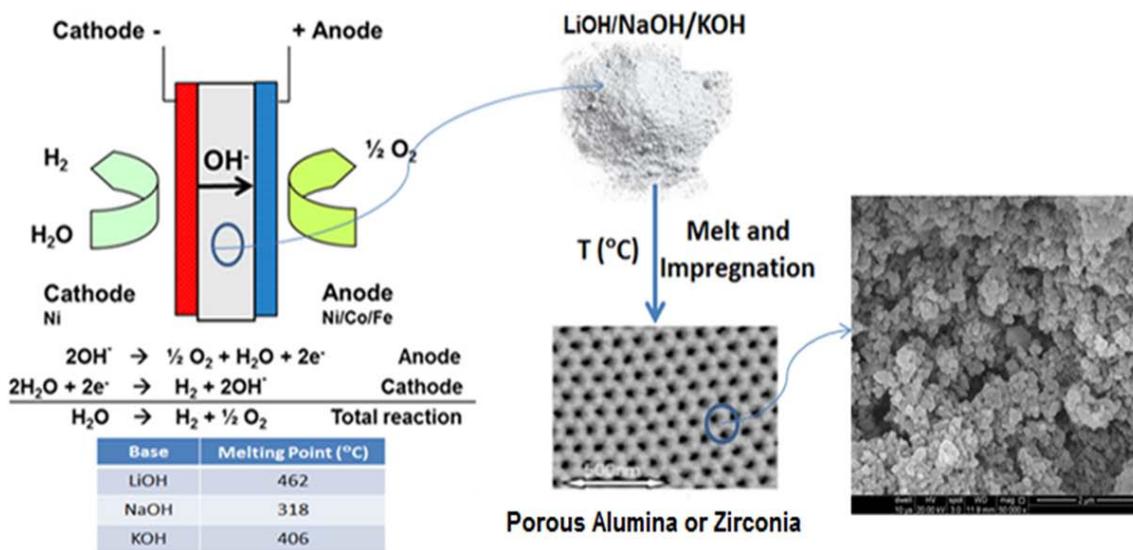


FIGURE 1. Technical approach to achieve high temperature alkaline water electrolysis

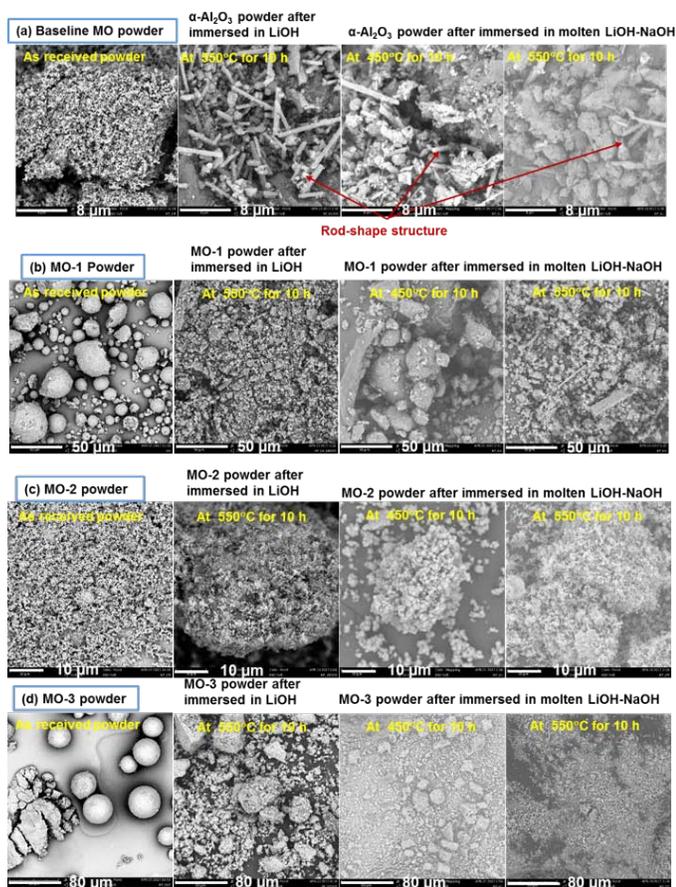


FIGURE 2. Surface morphologies of as received metal oxide powders and after immersion test of (a) baseline metal oxide, (b) MO-1, (c) MO-2, and (d) MO-3 materials, in LiOH and molten Li/Na hydroxide melts under air for 10 h

defined and no significant change in the particle/grain size occurred after performing the immersion test for 10 h in both LiOH and molten LiOH-NaOH melts. Indeed, the particle size of the MO-1, 2, and 3 powders remained constant and microstructure barely changed upon immersion in both LiOH and molten LiOH-NaOH melts.

Figure 3a shows the test apparatus, including a tubular furnace, gas flow arrangement, and sample placement within the furnace to oxidizing and reducing atmosphere exposure conditions. The sintered pellets of the single or eutectic composition of initial 25% hydroxide incorporated in the metal oxides were developed to measure the OH⁻ conductivity. Figure 3b shows the image of after-sintered pellets (13 mm diameter and thickness about 1 mm) of composite hydroxide electrolyte. The sintered pellets of mixed hydroxide and metal oxide were painted with silver paste and heated to ensure a good bond between the sample surface and silver paste. The temperature dependence of OH⁻ ion conductivities for the pelletized composite single/binary hydroxides is shown in Figure 3c. The single and binary hydroxides showed OH⁻ ion conductivity of 0.154 S.cm⁻¹

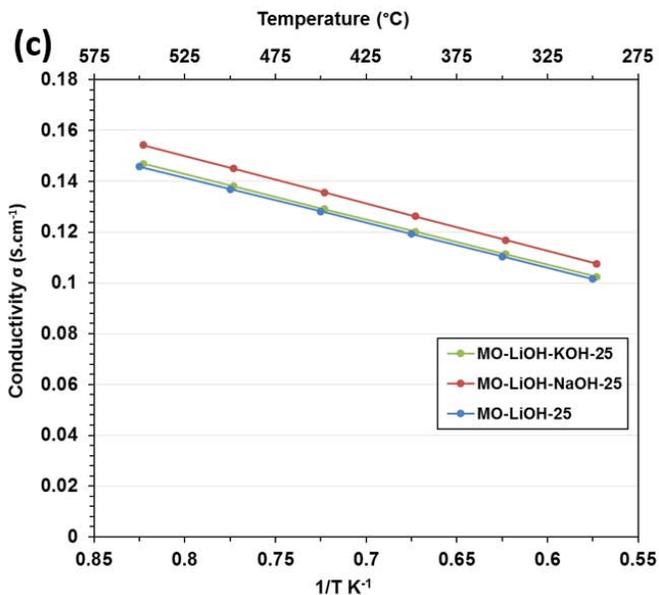
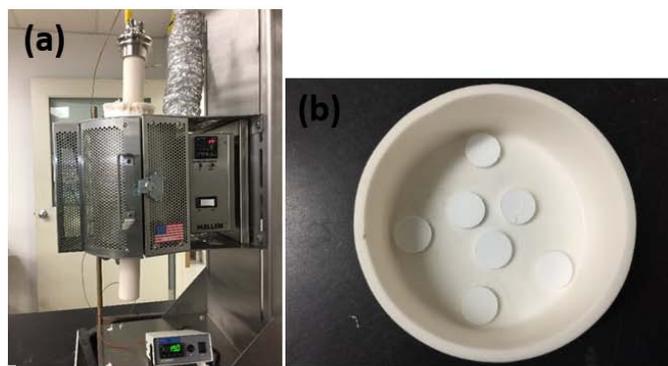
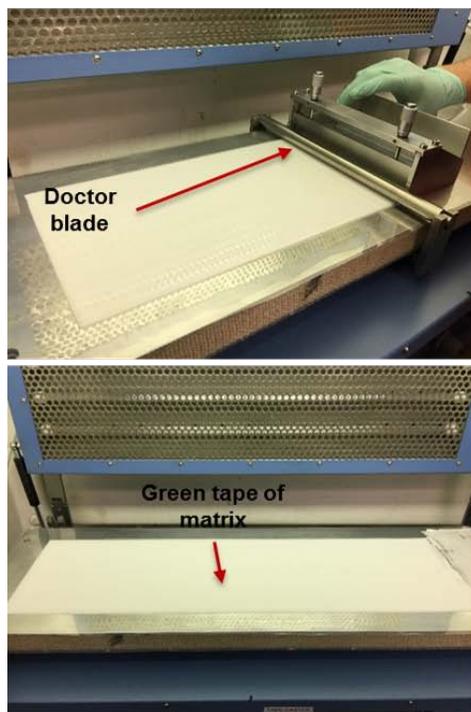


FIGURE 3. Photographs of (a) test assembly for OH⁻ conductivity measurement and (b) sintered single/binary hydroxide pellets, and (c) temperature dependence of the OH⁻ ion conductivity of single/binary hydroxides at 300°C–550°C in air atmosphere

and 0.142 S.cm⁻¹, respectively. The binary hydroxide conductivity was higher compared to that of single hydroxide at temperatures from 300°C to 550°C in air atmosphere. The loss of single/binary hydroxide content in the pellets was observed after testing at 550°C due to evaporation of low melting point of single (~400°C) or binary hydroxide (~300°C). The conductivity can be further improved by increasing the content of electrolytes in the porous matrices.

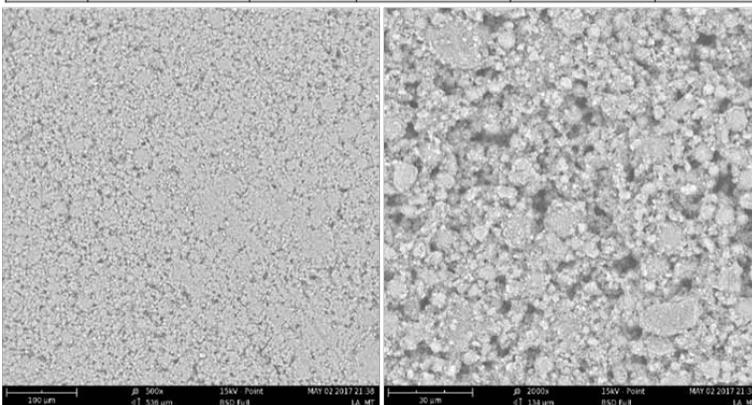
The lab scale-up development of the matrices has been initiated to optimize slurry formulation using a tape casting process. The selected matrices have been fabricated by the tape casting method. Figure 4 shows a picture of the lab-scale tape casting machine with heating system installed in the properties of the fabricated MO-1 matrix with thickness 0.50 mm, and scanning electron spectroscopy (SEM) images showing porous MO-1 after sintering at 550°C for 2 h in air atmosphere. The attained composite electrolyte has a porosity of 65% with average pore size of 0.1 μm.



Fabrication of green tape of matrix using doctor blade

Parameters of before and after sintered green sheet matrix

Matrix	Matrix Thickness (mm)		Solid content (%)		Porosity (%)	Pore size (µm)
	Green sheet tape	After sintered	before sintered	after sintered		
MO-1	0.60	0.50	69.78	66.57	65.426	0.096



SEM images of MO-1 after sintered at 550 °C for 2 h in air

FIGURE 4. Photograph of lab-scale tape casting machine with heating system installed in the hood (left); properties (table, upper right) and morphology (lower right)

CONCLUSIONS AND UPCOMING ACTIVITIES

- The short-term stability of different metal oxides in single and binary hydroxide melts has been evaluated, and stable metal oxides have been selected.
- OH- ion conductivities of the single/binary hydroxides impregnated in metal oxide matrices have been measured. Initial conductivity is higher than 0.1 S.cm⁻¹ with less than 20 wt% hydroxides.
- A lab-scale tape casting machine is used for the fabrication of the electrodes and electrolyte matrix and green tape of matrix. Good porosity and pore size of green tape of matrix have been demonstrated.

Experiments will be performed to increase the OH- conductivity of the composite electrolyte by increasing the content of hydroxides. The green tape of more different metal oxide matrices will be optimized via the tape casting method and subjected to high temperature sintering (>650°C). The characterization plan for sintered matrix also consists of surface analysis, Brunauer-Emmett-Teller surface area, pore size distribution, and porosity. The anode and cathode catalysts will be selected to construct electrolyzer cells to evaluate the electrochemical performance.

FY 2017 PUBLICATIONS/PRESENTATIONS

1. Hui Xu and Kailash Patil, “High Temperature Alkaline Water Electrolysis,” presented at the 2017 DOE Annual Merit Review and Peer Evaluation Meeting, Washington, DC, June 2017.

REFERENCES

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