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Quarterly Report on Node (FY2018_Q2): Advanced Electrode and Solid Electrolyte Materials for Elevated Temperature Water Electrolysis to Support UTRC HTE Project

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The team in Idaho National Laboratory (INL) has made a good progress towards the milestones in this program to support UTRC. This technical report highlights progress by the HydroGEN Super Proton-Conducting High Temperature Electrodes (SPC HTE) Materials Node Capability in the following areas: (1) measurements of conductivities of two BCZY electrolytes; and investigate their stability in moist conditions (50% H_2O, 200 hours), (2) development of PBSCF steam electrode in proton conducting SOEC button-cell device, (3) performance improvement by optimizing micro-structure of steam electrode to achieve the target in milestone, and (4) research plan for the next quarter, to support UTRC HTE project.

1. The measurement of conductivities of two BCZY electrolytes and stability test

INL has agreed to provide SPC electrolysis cell composition reference material data for water splitting based on solid electrolyte materials research being conducted by the SPC HTE node experts. SPC HTE electrolyte materials should exhibit high proton conductivity for hydrogen separation and also chemical stability for durable operation of the devices. The SPC node reference materials selection is based on extensive prior investigation of conduction behavior and phase stability in practical operation conditions. The node experts have completed studies for two different barium-cerate-zirconate perovskite oxides: (a) BCZYYb7111 ($BaCe_{0.7}Zr_{0.1}Y_{0.1}Yb_{0.1}O_3$) and (b) BCZYYb4411 ($BaCe_{0.4}Zr_{0.4}Y_{0.1}Yb_{0.1}O_3$), to understand their proton conduction properties when exposed to real working conditions, and durability against moisture pressures around 0.5 atm. The third composition of BZY20 ($BaZr_{0.8}Y_{0.2}O_3$) is excluded for further study because both BCZYYb7111 and BCZYYb4411 show stable conductivity in 50% H_2O, but BZY20 is well known as a low-conductivity electrolyte.

Preliminary efforts in Q1 had found that BCZYYb7111 electrolyte exhibits high proton conductivity and great potential in water splitting application, which is demonstrated by the small electrolyte resistance; however, due to chemical stability challenges in high pressure moist conditions, a more stable material may be needed to balance stability and performance. UTRC understands increasing the stoichiometric Zr content can improve the resistance against reaction between steam and perovskite structure, but it should be noted that higher Zr content impacts the ability to fabricate dense pellets or membranes. UTRC may not have this technical problem since plasma is used to produce a thin membrane. Currently the SPC HTE node experts use conventional ceramic fabrication approaches; hence sintering additives (e.g., NiO) may be added to promote densification by introducing a liquid phase in the sintering.

In Q2, the conductivity measurement of BCZYYb7111 and BCZYYb4411 electrolyte and the stability test in 50% H_2O condition have been completed. Figure 1(a) shows the temperature-dependence of electrical conductivities in humid air (~3% H_2O). As expected, BCZYYb7111 exhibits comparable conductivity values to the results in literature [1]. When the Zr content is increased from 0.1 in BCZYYb7111 to 0.4 in BCZYYb4411, the conductivities at the same temperature accordingly decrease. When these two electrolyte materials are fabricated into the electrolysis cell with thickness of, e. g. 20 μm, the ideal ohmic resistances are calculated to be 0.07 ohm cm^2 for BCZYYb7111 and 0.2 ohm cm^2 for BCZYYb4411 at 600 ^oC. Because the total cell resistance mainly consists of ohmic resistance from electrolyte and polarization resistance from steam electrode, the electrolysis performance is determined by electrolyte thickness and catalytic activity of electrode material.

The stability of these two electrolytes in humidified air (~50% H_2O) was examined by observing the conductivity change for 200 h. It is clear to see that both materials are rather stable in such high humidity. Based on this finding, we may proceed to study these two electrolytes in electrolysis cells at the same time to acquire the information such as hydrogen production rate, Faradic efficiency, and long-term stability; and the systematic comparisons are necessary to know the pros and cons for each material system.

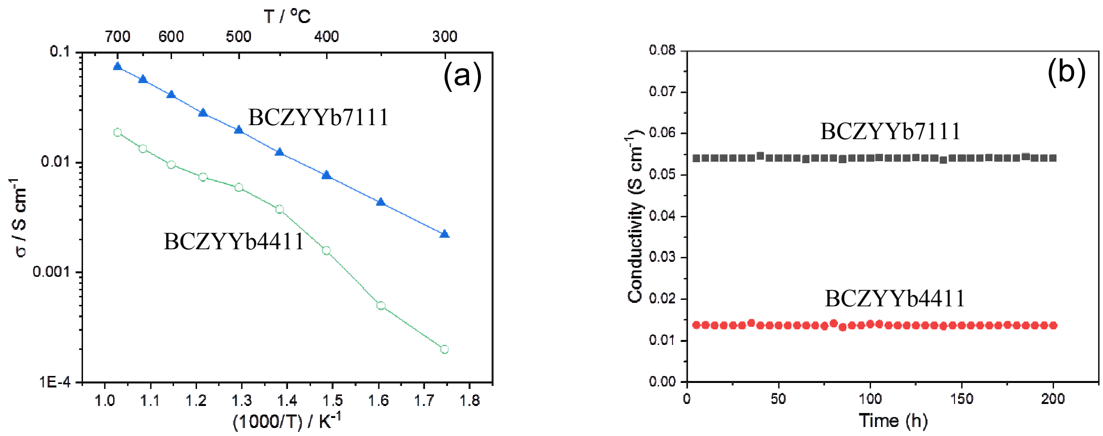

Figure 1. (a) The electrical conductivities of BCZYYb7111 and BCZYYb4411 electrolytes at different temperatures in humid air (~3% H_2O); (b) stability of material conductivity in 50% H_2O (carried by air) at 650 °C.

2. Hydrogen production performance based on proton-conducting electrolyte BCZYYb7111 and triple-phase conducting steam electrode $Pr(Ba_{0.5}Sr_{0.5})CoFeO_5$ (PBSCF)

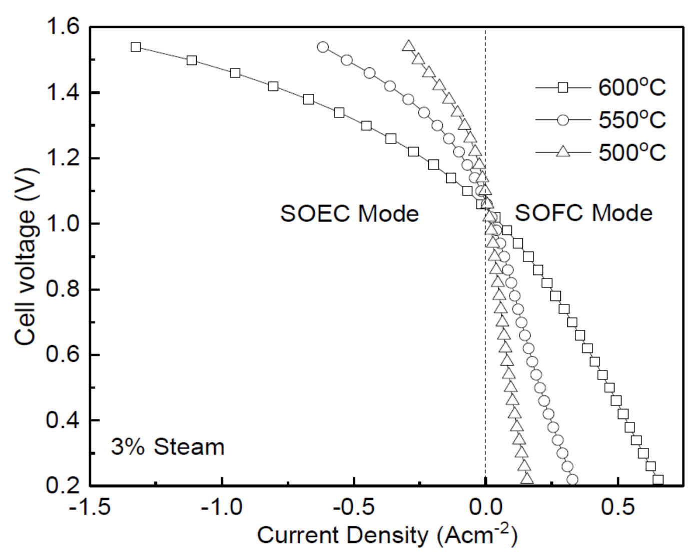

Figure 2. The current-voltage characteristic curves of Ni-BCZYYb7111/BCZYYb7111/PBSCF cell operated at 500-600 °C.

The electrochemical performance evaluation for the material system consisting of BCZYYb7111 electrolyte and steam electrode is critical to examine the feasibility of producing hydrogen at proposed low temperatures and the durability of chemical stability in practical operation. In this quarter, we've primarily measured the performance of electrolysis cells with BCZYYb7111 electrolyte and a triple conducting perovskite electrode material PBSCF, which showed very promising performance at proposed temperature and electrolysis voltage. Figure 2 shows the current-voltage curves of a button cell with structural configuration of Ni-BCZYYb/BCZYYb(~20μm)/PBSCF(~20μm) in both SOFC and SOEC modes at 500-600 ^{o}C, in which the positive current density refers to fuel cell operation while the negative current density corresponds to electrolysis cell operation. With 97% oxygen – 3% H_2O and pure H_2 introduced to steam electrode and hydrogen electrode respectively, the open-circuit voltage of the cell are 1.05, 1.07, and 1.9 V at 600, 550, and 500 ^{o}C. When the cell was operated at a fixed voltage of 1.4 V, the electrolysis current densities are -0.73, -0.33, and -0.16 A cm^{-2} at 600, 550, and 500 ^{o}C respectively.

3. Performance improvement by optimizing micro-structure of steam electrode

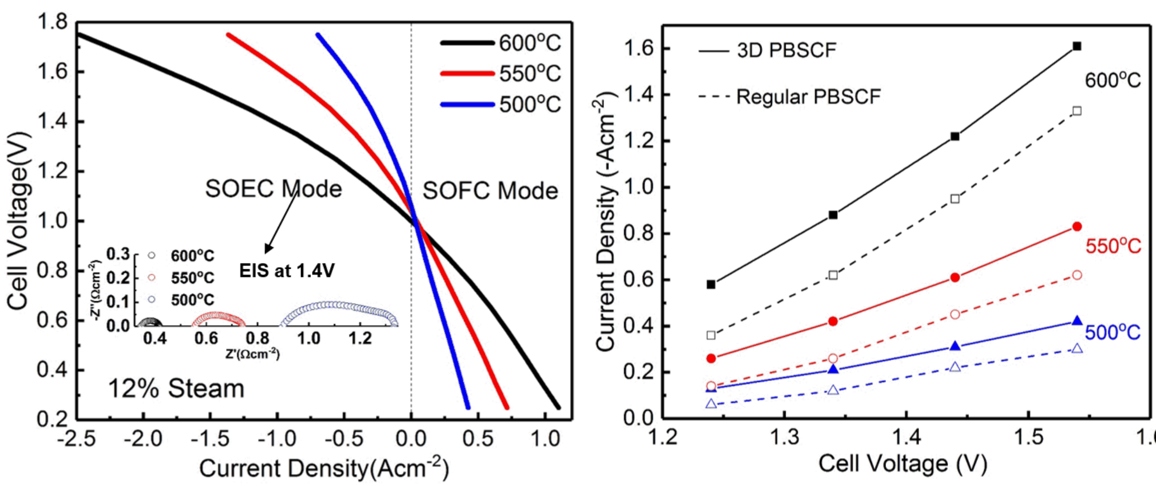

Figure 3. (a) The current-voltage curves of Ni-BCZYYb/BCZYYb/3D-PBSCF electrolysis cell at different temperatures; (b) the comparisons of the cells with regular and 3D PBSCF electrodes at different electrolysis voltages and operating temperatures.

The electrolysis performance can be further improved by constructing 3D self-architectured PBSCF electrode with optimal porous micro-structure for mass transfer. Figure 3a displays the electrochemical performance of an electrolysis cell with mesh-like electrode measured at a temperature range of 500 to 600 ^{o}C with a steam partial pressure of 12%. When the cell was operated at a potential of 1.4 V, the electrolysis current densities are −1.02, −0.4 and −0.2 A cm^{-2} at 600, 550 and 500°C, respectively. Therefore, the current density at 1.4 V has passed the program target of 1 A cm^{-2} at 600 °C. The results demonstrate the feasibility of applying this material system into metal-supported electrolysis cell platform.

The electrolysis performances between SOECs with regular and 3D-PBSCF steam electrodes are also compared in Fig. 3b to show the enhancement. In addition, to better understand the achievement we have made, the 3D-PBSCF electrode enabled SOEC was compared with the results in literature based on proton-conducting electrolysis cells, as shown in Table 1. To our best knowledge, this PBSCF electrode shows the highest current density at each temperature point.

Table 1. Comparison of hydrogen production performances of the proton-conducting SOECs in literature and this work.

Electrolyte	Steam electrode	Hydrogen electrode	T/ °C	Steam ratio	Applied Voltage/V	Current /Acm^{-2}	Ref.
BZCYYb	3D-PBSCF	Ni-BZCYYb	600 550 500	12%	1.4	1.02 0.4 0.2	This work
BZCYYb	Regular PBSCF	Ni-BZCYYb	600	12%	1.3	0.55	This work
$BaCe_{0.5}Zr_{0.3}Y_{0.2}O_{3-\delta}$ (BCZY)	$Sm_{0.5}Sr_{0.5}CoO_3$-BZCY	Ni-BZCY	600	50%	1.5	0.33	[2]
BZCYYb	$NdBa_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O_{5+\delta}$	Ni-BZCYYb	600	10%	1.3	0.75	[3]
$BaCe_{0.5}Zr_{0.3}Y_{0.16}Zn_{0.04}O_{3-\delta}$ (BZCYZ)	$La_{0.8}Sr_{0.2}Mn_{1-x}Sc_xO_{3-\delta}$	$La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-\delta}$ (LSCM)	700	5%	1.6	0.04	[4]
BCZYZ	Fe_2O_3-LSM-BCZYZ	LSCM-BCZYZ	800	5%	1.6	0.07	[5]
BCZYZ	LSCM-BCZYZ	Ni-BZCYZ	700	3%	1.3	0.78	[6]
$BaZr_{0.9}Y_{0.1}O_{3-\delta}$ (BZY)	$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF)-BZY	Ni-BZY	600	3%	1.3	0.05	[7]

The short-term durability was also examined by operating the electrolysis cell at a constant electrolysis voltage of 1.6 V for 78 hours. The electrochemical impedance spectra (EIS) results were acquired every 15 hours at a voltage of 1.6 V. As shown in the figure, the electrolysis current presents no degradation during the entire 78-hour steam electrolysis process. Instead, the SOEC with 3D steam electrode was constantly "activated" over the time since the current density increased steadily. According to the EIS results, the cell total resistance showed a drop from 1.0 to 0.88 Ω cm^2 within the initial 15 hours and then gradually decreased to 0.85 Ω cm^2 after 75 hours.

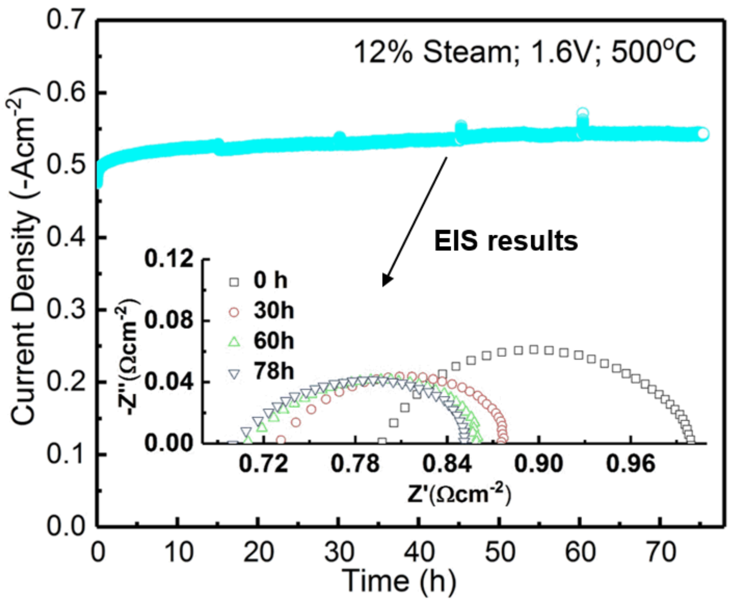

Figure 4. The short-term stability test of current density at applied voltage of 1.6 V at 500°C, which demonstrates constant activation in electrolysis process. EIS results at different period of time are inserted. H_2 and 12% H_2O–88% O_2 are used as the reacting gases in hydrogen electrode and steam electrode, respectively.

The results demonstrate the reliability of material system including the BCZYYb7111 electrolyte and PBSCF steam electrode in the practical electrolysis conditions, and also stability of electrode/electrolyte interface.

The Faradaic efficiencies at different electrolysis voltages were obtained by calculating the ratio of actual hydrogen generation rate to theoretical hydrogen production rate. As shown in Table 2, the Faradaic efficiencies are very high when the voltage varies from 1.2 V to 1.8 V. The high efficiencies indicate the little loss of electricity input for this material system with high conductive BCZYYb7111 electrolyte and highly active 3D-PBSCF steam electrode.

Table 2. Faraday efficiency at different applied voltages at 500 °C.

Applied voltage / V	**1.2**	**1.4**	**1.6**	**1.8**
Current density/Acm^{-2}	0.07	0.23	0.49	0.84
Faraday efficiency / %	99.6	98.4	98.0	97.5

While the proton-conducting SOEC based on BCZYYb7111 shows great potential to be applied into metal-supported SOEC system, we will still investigate more stable and less-performing BCZYYb4111-based electrolysis cells in the next quarter to compare the differences between two series of material systems.

3. Research Plan

In the next quarter, the node experts will continue the tasks listed in the milestones:

- Study the electrochemical performances of BCZY4411 electrolyte based SOEC with PBSCF electrode, and evaluate the stability of hydrogen production in electrolysis cell, and report the results to UTRC;
- Faradaic efficiency will be measured to compare with the results of BCZY7111 based SOEC;
- Measure the performance of one-inch metal-supported SOEC from UTRC.

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