Pacific Northwest
NATIONAL LABORATORY

PNNL-29240

Tailored Syngas via High Temperature H2O-CO2 Co-Electrolysis

October 2019

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U.S. DEPARTMENT OF ENERGY

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

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Abstract

This project has developed a new testing capability at PNNL and has evaluated solid oxide electrolysis cell (SOEC) materials for the ability to co-electrolyze carbon dioxide and steam to produce synthesis gas.

CO_2-H_2O co-electrolysis, the simultaneous electrochemical reduction of carbon dioxide and steam, was performed on the porous Ni-based electrodes in high temperature SOECs. Experiments were conducted using small button cells and the rate of the electrochemical reactions was measured at 750oC for varied reactant compositions: 10-98%CO_2 and 5-50% H_2O, also in the presence of some H_2 and CO to ensure reducing environment and avoid Ni oxidation.

Prior to executing the experiments, a new Standard Operating Procedure (SOP) was developed and implemented for testing button cells in CO2, in addition to the existing SOP enabling testing of button cells in standard steam electrolysis mode. New safety features – a thermocouple-based limit controller, multiple sensors and solenoid shutoff valves – were purchased, assembled and installed to create the automated circuit, controlling gas shutoff (Figure 1). This has aided in establishing PNNL capabilities in co-electrolysis testing.

Acknowledgments

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1.0 Introduction and Project Description

SOECs are used to split water at high temperatures using low cost surplus renewable or nuclear electrical energy and heat and convert it to chemical energy which is stored in H_2 and O_2. SOECs can also be used for the co-electrolysis of steam and carbon dioxide. The two reactants, typically waste products in an industrial plant, could be turned into synthesis gas (syngas, $CO+H_2$), a valuable and commonly used reagent in the chemical industry. Syngas is used to produce synthetic fuels, olefins or other liquid hydrocarbons via Fischer-Tropsch synthesis or for methanol, ethanol or DME synthesis. In addition, high temperature CO2 electrolysis to CO can be performed in SOECs as well (Haldor Topsøe, 2018).

The high efficiency operation of a SOEC device has been demonstrated by the OxEon team, Haldor Topsoe and others. The high efficiency is derived from the inherent heat recuperation of resistive losses to provide a portion of the energy required for the endothermic electrolysis reaction

2.0 Accomplishments

- New system controls for box furnaces were designed, assembled and tested to allow unattended operation during long-term experiments and to prevent a) accumulation of carbon monoxide inside the hydrogen electrode chamber at low temperatures in event of loss of power, and b) oxidation of fuel electrodes in event of loss of hydrogen supply.

- A baseline SOEC cell performance in different CO_2-H_2O mixtures (also in the presence of some H_2 and CO to prevent Ni oxidation in pure H_2OCO_2) was established during 70 hours of continuous testing. Kinetics of electrochemical CO_2 reduction were evaluated at 750^oC for varied CO_2/H2O ratios and compared to steam electrolysis. The rate of electrolysis changed as H_2O > H_2O-CO_2 > CO_2.

- The ability to control H_2 :CO ratios in generated syngas by varying the inlet H_2O/CO_2 ratios was demonstrated.

3.0 Results

All button cells used in this project were fabricated inhouse previously using standard SOFC materials. The SOEC cells were consisted of a dense yttria-stabilized zirconia (YSZ) electrolyte, Ni-YSZ hydrogen electrode, (La,Sr)(Co,Fe)O_3 (LSCF) oxygen electrode, and doped ceria barrier layer between the oxygen electrode and the YSZ electrolyte. The tests were performed at 750°C at a fixed voltage of 1.1 Volt. Electrochemical performance of the cells was recorded in time continuously using multichannel potentiostat, with occasional attended interruptions to obtain current voltage characteristics (I-V plots) and collect the impedance spectra. Electrochemical impedance spectroscopy was used to separate losses in each cell associated with ohmic and electrodic processes while varying current density and reactant compositions and also to monitor the changes in cell resistances in time to elucidate the degradation mechanism. Open-circuit voltage was periodically recorded in time to verify the quality of seals in high steam environment as well as the consistency in steam production.

All cells were initially tested for 50 hours in SOFC mode to establish a steady-state and compare the electrode activity to previously tested cells. From approx. 50 to 200 hours (Figure 2) and then again for 20 hours at approx. 300 hour mark cells were tested in steam electrolysis mode at 1.1 Volt and H_2O:H_2=1:1. After that cells were operated at 1.1 Volt in co-electrolysis mode at H_2O:CO_2:H_2:CO=1:2:0.8:1. Hydrogen sensor malfunction prevented cell testing between 200 and 300 hours. From approximately 350 hours, 2 cells were operated in practically pure CO_2 with only 2-3 per cent of H_2 added to provide reducing environment and avoid Ni oxidation. At these temperatures, Ni oxidizes to NiO at pO_2~10^{-14} atm, while pure CO_2 results in pO_2~10^{-7} atm.

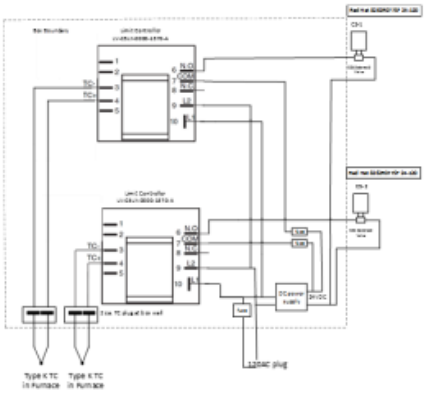

Figure 1. Diagram of the circuit controlling CO_2 shutoff.

As shown in Figure 2, no rapid change in degradation slope occurred during co-electrolysis. Cell performance in 50% H_2O-CO_2 at 1.1 V appeared to be lower than in 50% H_2O because the open-circuit was lower and because there is a thermodynamic advantage for steam electrolysis at 750°C. As shown in Figure 3, higher energy requirements were needed for both CO_2 and co-electrolysis as compared to steam electrolysis. For 0.5 A/cm^2 , cell overpotential was 70 mV higher for co-electrolysis and 170 mV higher for pure CO_2 electrolysis. In principle, the equilibrium potentials for reduction of CO_2 to CO and H_2O to H_2 become close at higher temperature, 800°C. Our work shows that at 750°C steam preferentially reacts, per thermodynamic predictions, and also likely because of kinetic issues (Figure 4). CO_2 has a strong dipole moment, but is linear and may not be as easily adsorbed. The mechanism of CO_2 reduction must be more complex than H_2O splitting. Yet, SOEC cells were active in both steam and CO_2 electrolysis (Figure 3). In addition to electrochemical reduction, CO_2 could also be converted to CO via reverse water gas shift reaction:

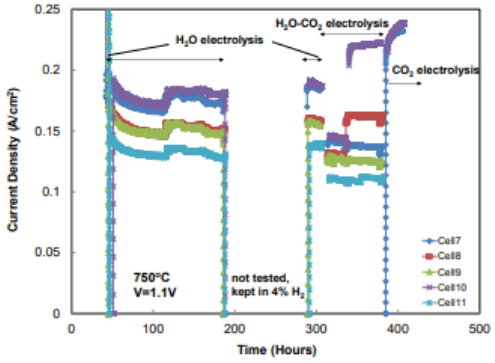

Figure 2. Five cell performance in steam electrolysis mode, in co-electrolysis mode, and in CO_2 electrolysis mode. In steam electrolysis, H_2O/H_2=50/50. In Co-electrolysis, (CO_2+H_2O)/(H_2+CO)=50/50. In CO_2 electrolysis, CO_2/H_2=98/2.

$CO_2+H_2=CO+H_2O$.

No degradation was observed when SOECs were tested for 20 hours in nearly pure carbon dioxide, with minimal hydrogen added. Moreover, a slight, so far unexplained, performance increase in time was observed during testing in CO_2.

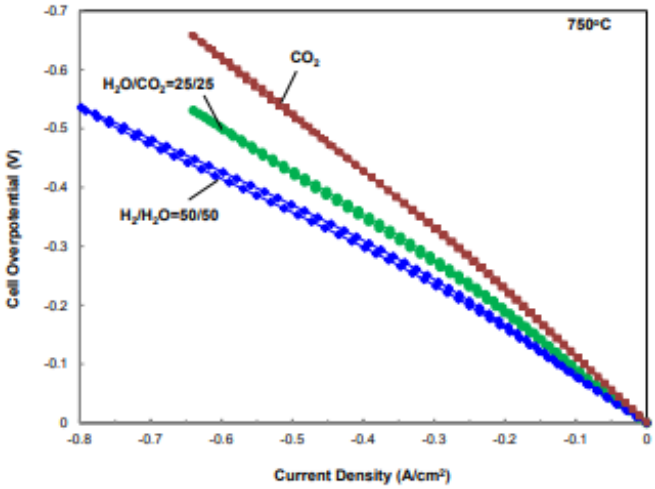

Figure 3. Overpotential required to conduct steam electrolysis, co-electrolysis and CO_2 electrolysis at 750°C (cell10 data).

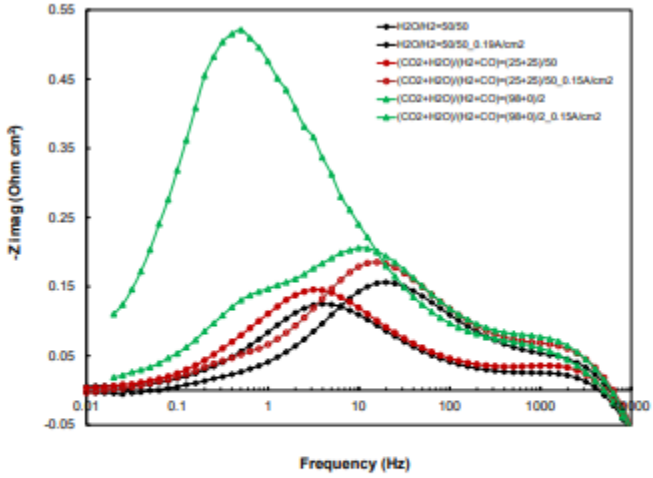

Figure 4. Impedance spectra obtained at 750°C in H_2O-H_2 (black) and H_2O-CO_2 mixes (red and green) with varied CO_2-to-H_2O ratios, indicating mass limitations in the presence of CO_2 at polarization (open symbols) and at zero current (closed symbols).

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