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Demonstration of direct conversion of CO₂/H₂O into syngas in a symmetrical proton-conducting solid oxide electrolyzer

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ABSTRACT

We have previously reported the electrochemical reduction of CO₂ to CO with simultaneous steam electrolysis in a proton conducting solid oxide electrolyzer (PCSOE); however, the conventional Ni-cermet electrode is rapidly oxidized by H₂O/CO₂ in cathode that causes cell performance degradation. In this work, we report a novel symmetrical PCSOE with redox-stable LSCM ((La_{0.75}Sr_{0.25})_{0.95}Cr_{0.5}Mn_{0.5}O_{3-δ}) electrode for the electrochemical conversion of CO₂/H₂O into syngas (CO/H₂). The Ru catalyst is impregnated to LSCM to improve electrode activity. Electrochemical measurements demonstrate that the CO₂ is electrochemically reduced to syngas (CO/H₂) with simultaneous steam electrolysis. The loading of Ru catalyst promotes the electrochemical process with higher Faradic efficiency while induces a more competitive process of hydrogen evolution at 700 °C.

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Introduction

Proton-conducting solid oxide electrolyzers (PCSOEs) are attracting more and more attentions because of the kinetic and thermodynamic advantages at intermediate to high temperatures (500–1000 °C) [1–3]. The electrical energy demand decreases when increasing the system operation

temperature. In addition, overvoltages at both anode and cathode can be effectively reduced at high temperatures. It has been interestingly demonstrated that PCSOE could achieve electrochemical carbon dioxide reduction with steam electrolysis to produce oxygen in anode and valuable fuel in cathode [4–11]. The electrochemical reactions involved in PCSOEs for CO₂/H₂O conversion can be expressed as:

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Anode:



Cathode:



Protons (H^+) from steam electrolysis transport through electrolyte from anode to cathode and *in situ* electrochemically reduce CO_2 into syngas (H_2/CO) which is the feedstock of Fischer-Tropsch (F–T) synthesis [12]. Combination of PCSOEs for syngas production with F–T process would be a feasible choice to simultaneously produce hydrocarbon fuels, which is capable of avoiding major infrastructure shift that would be otherwise required for a pure H_2 or CO-based transportation system. The produced hydrocarbon or liquid fuels by solid oxide technology can make a big step in the industry field with the reduced CO_2 emission. Similarly, the electrochemical reduction of NO_x and N_2 have also been successfully realized in proton-conducting electrolyzers. The proton in cathode can *in-situ* electrochemically reduce the NO_x and N_2 into N_2 and even NH_3 [13–15].

In a PCSOE, the feed gases in cathode contain a certain amount of CO_2 or pure CO_2 for electrochemical reduction while the anode is exposed to steam for electrochemical oxidation. The oxygen partial pressure (p_{O_2}) at cathode side is higher than that of solid oxide fuel cell anode with H_2 gas. The reduction of CO_2 produces H_2O that combines with CO_2 to make a $\text{CO}_2/\text{H}_2\text{O}$ atmosphere. Therefore, material stability under the mixture gas atmosphere has to be fit for cathode in PCSOEs. Our previous work has demonstrated that the traditional Ni cathode is easily oxidized by $\text{CO}_2/\text{H}_2\text{O}$ atmosphere in cathode that degrades the performance of solid oxide electrolyzer [10]. Redox-stable oxide material seems to be preferred for cathode since there is a possible oxidation degradation for metallic cathode under the weak oxidizing or less reducing atmospheres. Materials used as oxygen electrodes in PCSOEs have also to be noted for this issue since steam is the main component in the feed gases at anode side in PCSOEs. Diffusion processes as well as polarization resistance of H_2O , CO_2 and other intermediates probably play an important role in the steam oxidation or carbon dioxide reduction [3,7,8,12,16]. As the same manner in solid oxide fuel cell, high conductivity is required for electrode materials in PCSOEs and mixed conductors (O^{2-} and e^-) are preferable as well.

There are limited experimental studies of PCSOEs for $\text{CO}_2/\text{H}_2\text{O}$ conversion in the literatures [4–11,17–19], especially focusing on the cathode materials. In this work, we explore a symmetrical PCSOE with LSCM ($(\text{La}_{0.75}\text{Sr}_{0.25})_{0.95}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$) as both anode and cathode for direct CO_2 reduction with simultaneous steam electrolysis. Perovskite LSCM is a redox-stable ceramic material with high electro-catalytic activity [20,21] and has been used as cathode in solid oxide

electrolyzers [22,23]. Although traditional Ni is an excellent cathode electro-catalyst; however, the oxidation of Ni to NiO/Ni(OH) $_2$ amorphous mixtures degrades cathode activities and electrolysis performances as reported in our previous work [24]. In this work, the $\text{BaCe}_{0.5}\text{Zr}_{0.3}\text{Y}_{0.16}\text{Zn}_{0.04}\text{O}_{3-\delta}$ (BCZYZ) is used as a proton conducting electrolyte, which has also been recognized as a promising electrolyte with high chemical stability against $\text{CO}_2/\text{H}_2\text{O}$ [25].

In this work, a proton conducting solid oxide electrolyzer with a configuration of LSCM-BCZYZ|BCZYZ|BCZYZ-LSCM has been prepared. Direct CO_2 reduction in cathode with simultaneous steam oxidation in anode has been performed at 700 °C. The Ru catalyst is then impregnated in LSCM to improve electrode activity for the enhancement of CO_2 reduction. Electrochemical evaluation is then systematically performed.

Experimental

Proton-conducting electrolyte $\text{BaCe}_{0.5}\text{Zr}_{0.3}\text{Y}_{0.16}\text{Zn}_{0.04}\text{O}_{3-\delta}$ (BCZYZ) powders were synthesized by a modified glycine-nitrate combustion process with the final treatment at 1150 °C for 2 h in air [19]. The $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$ (LSCM) powders were synthesized via a combustion method while the final treatment temperature was at 1000 °C for 3 h in air [26]. X-ray diffraction studies (Stone, CuK α 1, Transmitting mode, 2 min^{-1}) were performed to confirm the phase formation of BCZYZ and LSCM. High-resolution transmission electron microscopy analysis (HR-TEM) (JEM-2100F, JEOL, Japan) with selected area diffraction was performed to observe the oxidized and reduced LSCM powders. X-Ray Photoelectron Spectroscopy (XPS) (ESCALAB25, Thermo, USA) was performed to analyze the oxidized and reduced LSCM powders.

About 2.0 g LSCM powders were pressed into a bar followed by sintering at 1400 °C (3 °C min^{-1}) for 10 h in air for conductivity tests which were performed in air using the DC four-terminal method with temperature ranging from 25 to 800 °C (Keithley 2000, Digital Multimeter, Keithley Instrument Inc, USA). The conductivities were recorded versus temperature with an online system at a temperature step of 0.5 °C. The dependence of conductivity on p_{O_2} was tested at 800 °C with p_{O_2} ranging from 10^{-2} to 10^{-18} atm. The p_{O_2} was changed by flowing 5% H_2/Ar at the flow rate of 1 ml min^{-1} and recorded using an online sensor (Type 1231, oxygen sensor, Noveltch, Australia).

The 1-mm-thick BCZYZ disc electrolyte support was prepared by dry-pressing BCZYZ powder into a green disk with a diameter of 20 mm followed by a high-temperature sintering in air at 1400 °C for 5 h. The LSCM and BCZYZ powders at weight ratio of 65:35 were mixed and then prepared into electrode slurry [25]. The two electrodes were screen printed onto two surfaces of electrolyte in a symmetric positions with an area of 1 cm^2 followed by heat treatment at 1150 °C (2 °C $\cdot \text{min}^{-1}$) for 3 h to assemble a cell in a configuration of LSCM-BCZYZ|BCZYZ|BCZYZ-LSCM. The Ru catalyst was impregnated into LSCM electrode to enhance the electrode activity while the loading is 0.5% in weight ratio. The current collection layer was constructed with silver paste, which was

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