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Composite oxygen electrode LSM-BCZYZ impregnated with Co_3O_4 nanoparticles for steam electrolysis in a proton-conducting solid oxide electrolyzer

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ABSTRACT

A composite oxygen electrode based on Co_3O_4-loaded $La_{0.8}Sr_{0.2}MnO_3$ (LSM)-$BaCe_{0.5}Zr_{0.3}Y_{0.16}Zn_{0.04}O_{3-\delta}$ (BCZYZ) is investigated for steam electrolysis in a proton-conducting solid oxide electrolyzer. The conductivity of LSM is studied with respect to temperature and oxygen partial pressure and correlated to the electrochemical properties of the composite oxygen electrodes in symmetric cells and solid oxide electrolyzers at 800 °C. The optimal Co_3O_4 loading in the composite oxygen electrode is systematically investigated in symmetric cells; loading catalytically active Co_3O_4 significantly enhances the electrode performance, unlike the bare LSM-BCZYZ electrode. Steam electrolysis was then performed using LSM-BCZYZ and 6 wt.% Co_3O_4-loaded LSM-BCZYZ oxygen electrodes, respectively. The Co_3O_4-loaded catalyst significantly improves the electrode process and enhances the current density below a certain applied voltage. The current efficiencies reach approximately 46% with a 10% H_2O/air feed for the oxygen electrode.

1. Introduction

Hydrogen attracts research interest because it may be created using renewable resources before storage and transportation; moreover, it is an environmentally friendly source of energy [1–6]. There are many sources used to produce hydrogen, including fossil fuels, biomass, and electrochemistry. From a long-term perspective, using water (steam) electrolysis ($H_2O \rightarrow H_2 + 1/2O_2$) in a solid oxide electrolyzer (SOE) to produce hydrogen has become more popular because the high temperature contributes energy to the steam dissociation, leading to favorable kinetic and thermodynamic properties [7–12].

Proton-conducting solid oxide electrolyzers (SOE) are inverted proton-conducting solid oxide fuel cells (SOFC); they convert electrical energy directly into chemical energy [13–16] and can efficiently produce pure hydrogen via high temperature steam electrolysis. Using external electricity, steam is split into oxygen and protons. The protons diffuse across the proton-conducting electrolyte to the fuel electrode, where pure hydrogen forms from protons with in the three-phase boundary. Hydrogen formation only occurs in the fuel

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electrode compartment, making it unnecessary to separate the hydrogen from the steam.

In a proton-conducting solid oxide electrolyzer, the oxygen electrode is under strongly oxidizing conditions during the steam electrolysis, conditions under which a purely redox active metal cannot operate. Stable oxygen electrode materials with efficient catalytic performances must still be developed. We have recently reported a composite oxygen electrode based on $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$, $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ and $(La_{0.75}Sr_{0.25})_{0.95}Mn_{0.5}Cr_{0.5}O_{3-\delta}$ for direct steam electrolysis in a proton-conducting solid oxide electrolyzer [15,16]. However, the electrode polarization resistance of the electrolyzer is still considerable, and the steam electrolysis remains limited by the kinetics processes of the electrode. Enhancing the electro-catalytic performance of the electrode is an effective way to improve the electrolytic process. Co_3O_4 is reportedly an efficient electro-catalyst for oxygen evolution reactions (OER) in metal-air batteries [17–19] and alkaline water electrolyzers [20–22]. In the oxygen electrode of a proton-conducting electrolyzer, the H_2O molecules are split into O^{2-} ions and protons under an external electrolysis potential, and the O^{2-} ions are oxidized to O_2 gas before being released from the electrode. This process is also a typical oxygen evolution reaction that occurs on the electrode of an electrolyzer. Therefore, a Co_3O_4 electro-catalyst might equally enhance the electrode electro-catalytic performance of an electrolyzer.

In this work, composite electrodes based on LSM-BCZYZ and Co_3O_4-loaded LSM-BCZYZ are systematically investigated as oxygen electrodes for steam electrolysis in proton-conducting solid oxide electrolyzers. The electrical conductivity of $La_{0.8}Sr_{0.2}MnO_3$ is studied with respect to temperature and oxygen partial pressure and correlated to the electrochemical properties of the composite oxygen electrodes in the symmetric cells and solid oxide electrolyzers. The electrochemical performance of the composite electrodes based on LSM-BCZYZ and Co_3O_4 catalyst-loaded LSM-BCZYZ are systemically studied in proton-conducting solid oxide electrolyzers for steam electrolysis.

2. Experimental

The $La_{0.8}Sr_{0.2}MnO_3$ powder was synthesized using a solid-state reaction with an appropriate mixture of La_2O_3, $SrCO_3$ and MnO_2 powders. The mixture was ball-milled in acetone before being dried and pressed into pellets at room temperature; subsequently, the material was treated at 1400 °C for 10 h in air. The pellets were then ground, repelletized and fired at same temperature for 10 h in air. The LSM powder loaded with 10 wt.% Co_3O_4 was generated by impregnating the LSM powder with a $Co(NO_3)_2$ solution followed by a heat treatment at 500 °C for 30 min in air. All of the reagents (Chemical grade) were purchased from the SINOPHARM Chemical Reagent Co., Ltd (China). X-ray diffraction (Rigaku, Japan) was conducted to analyze the phase formation of the LSM and Co_3O_4-loaded LSM powders. Appropriate amounts of the LSM powders were pressed into a bar, followed by a 10 h heat treatment at 1400 °C in air before the conductivity test. The relative sample density reached 76%. Conductivity tests were performed in air using the dc four-terminal method from room temperature to 800 °C; conductivity was recorded versus temperature with an online system in 0.4 °C steps. The relationship between conductivity and oxygen partial pressure was tested at 800 °C with oxygen partial pressures ranging from 0.2 to 10^{-20} atm, which were adjusted by flowing dry 5% H_2/Ar at 20 ml min^{-1}.

$BaCe_{0.5}Zr_{0.3}Y_{0.16}Zn_{0.04}O_{3-\delta}$ (BCZYZ) was synthesized using a solid-state reaction method. The mixture of $BaCO_3$, CeO_2, ZrO_2, Y_2O_3 and ZnO powders was ball-milled at room temperature and subsequently fired at 1300 °C in air for 10 h. A 2-mm-thick BCZYZ disc for an electrolyte support was prepared by dry-pressing the BCZYZ powders into a green disk with a 20 mm diameter before sintering at 1400 °C for 10 h. The composite oxygen electrode slurry was prepared by milling LSM with BCZYZ (60:40 in weight ratio) in alpha-terpineol with the proper amount of cellulose additive. Similarly, the composite fuel electrode slurry was prepared using NiO and BCZYZ (60:40 in weight ratio) with the method described above. The solid oxide symmetric cell and solid oxide electrolyzer with LSM-BCZYZ/BCZYZ/LSM-BCZYZ and LSM-BCZYZ/BCZYZ/NiO-BCZYZ configurations were coated with electrode slurry in symmetrical positions on electrolyte supports within a 1 cm^2 area followed by an appropriate heat treatment (1400 °C for the NiO-BCZYZ electrode; 1100 °C for the LSM-BCZYZ electrode) for 3 h in air. Different contents of Co_3O_4-loaded LSM electrodes were achieved by impregnating the LSM electrodes with an appropriate $Co(NO_3)_2$ nitrate solution several times, with a 30 min heat treatment at 500 °C in air after each impregnation. The maximal content of each impregnation treatment was 2 wt.%. Silver paste was printed onto both electrode surfaces followed by a 500 °C heat treatment (3 °C·min^{-1}) for 30 min in air for current collection. Silver electrical wire (0.2 mm in diameter) was then connected to both current collectors using silver paste followed by firing at 500 °C (3 °C·min^{-1}) for 30 min in air. The microstructures of the LSM-BCZYZ and 6 wt.% Co_3O_4-LSM electrodes of the symmetric cell were observed with a scanning electron microscope (SEM, SU8020, HITACHI, Japan). The LSM-BCZYZ electrode symmetric cell and the Co_3O_4-loaded LSM-BCZYZ electrode symmetric cells with different Co_3O_4 contents were tested at different applied current densities in air, as well as under different oxygen partial pressures under OCV conditions, at 800 °C using an electrochemical workstation (IM6, Zahner, Germany). All of the gas flow rates were maintained at 30 ml·min^{-1} with a mass flow meter (D08-3F, Sevenstar, Beijing, China).

The LSM-BCZYZ (40%) and (LSM-BCZYZ (40%))-Co_3O_4 (6 wt.%) powders were produced by ball-milling LSM and BCZYZ powders followed by the appropriate impregnation treatment. The specific surface area (SSA) of these powders was characterized by BET (Brunauer, Emmett and Teller) measurements (SA 3100, Beckman Coulter).

The solid oxide electrolyzers based on the LSM-BCZYZ and 6 wt.% Co_3O_4-loaded LSM-BCZYZ oxygen electrodes were sealed onto homemade testing jigs using ceramic paste (JD-767, Jiudian, Dongguan, China) for the electrochemical measurements. The electrolyzers were typically tested at 800 °C with 5% H_2/Ar at 30 ml·min^{-1} fed into the fuel electrode and 10% H_2O/Air (saturated steam concentration at 46 °C [23]) at 30 ml·min^{-1} introduced to the oxygen electrode for

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