Reversibly *in-situ* anchoring copper nanocatalyst in perovskite titanate cathode for direct high-temperature steam electrolysis

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ABSTRACT

This paper investigates a potential cathode material $(La_{0.2}Sr_{0.8})_{0.9}Ti_{0.9}Cu_{0.1}O_{3-\delta}$ (LSTCO) with A-site deficiency and B-site excess which was designed as a parent material for anchoring exsolved copper nanocatalyst on the surface of $La_{0.2}Sr_{0.8}TiO_{3+\delta}$ (LSTO) through a high-temperature reduction. Physical characterization of the samples by combined use of X-ray diffraction, scanning electron microscope, energy-dispersive spectroscopy, thermogravimetric analyzer and X-ray photoelectron spectroscopy indicated that the exsolution and dissolution of the Cu nanoparticles in the cathode was completely reversible in the redox cycles. Electrical properties of LSTO and LSTCO were systematically investigated which correlated closely with electrochemical performance of the composite electrodes in symmetrical cells and electrolysis cells. Polarization resistance (R_p) of the symmetrical cells was improved from $3\ \Omega\ cm^2$ of the LSTO to $1.5\ \Omega\ cm^2$ of the LSTCO in hydrogen atmosphere at 800 °C. Current efficiencies of the solid oxide electrolyzer with Cu-anchored LSTO cathode were found to be enhanced by approximately 20% compared to the bare cathode with or without reducing gas flowing over them under the applied voltage of 2.0 V at 800 °C, respectively.

1. Introduction

With the aggravation of global warming and climate change problems caused by production and consumption of fossil fuels, more and more research attention has been turned to clean and renewable resources [1–5]. Hydrogen has now been considered as a future leading fuel though it is not a major fuel at the moment [6,7]. Steam electrolysis is a promising method to produce hydrogen because the high-temperature heat in the process offers part of the energy for steam dissociation accompanied with favorable kinetics and thermodynamics [8–10]. Recently, solid oxide electrolyzers (SOEs) have attracted a great deal of interests owing to their unique properties in terms of directly and efficiently converting electrical energy into chemical fuel energy. An oxide-ion-conducting solid

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oxide electrolyzer can electrolyze steam into hydrogen and oxygen under external electrolysis potential. Steam molecules are electrochemically reduced to H_2 at the cathode side by applying external potential while the O^{2-} ions are transported through the oxide-ion-conducting electrolyte to the anode compartment where oxygen is formed and released [11–15].

Up to now, most studies have focused on the preferential use of Ni-YSZ as the cathode of the oxide-ion-conducting solid oxide electrolyzer for the high-temperature steam electrolysis. However, the inherent redox instability of Ni-YSZ remains an unsolved problem and a significant concentration of hydrogen has to be fed at the cathode to prevent the oxidation of Ni into NiO in the process of steam electrolysis for hydrogen production. Otherwise, the oxidation of the Ni in this process may lead to a loss of the electrical conductivity, degradation of the electrode performance and even delaminations of the electrode layer from the electrolyte surfaces [16–19]. In contrast to Ni-YSZ, the perovskite-type $La_xSr_{1-x}Cr_yMn_{1-y}O_{3-\delta}$ (LSCM) is an active and redox-stable material which has attracted a lot of attentions in the high-temperature solid oxide fuel cell (SOFC) field [20,21]. Recently, Irvine et al. reported that direct steam electrolysis with the LSCM-SDC composite cathode had demonstrated promising performance and long-term stability even without reducing gas flowing over the composite electrode [22,23]. However, the p-type conduction mechanism of LSCM is not well adapted to the strong reducing potential which inevitably produces large electrode polarization resistance and the strong reducing potential causes chemical and structural changes of the LSCM cathodes as well [7]. Compared to LSCM, perovskite $La_xSr_{1-x}TiO_{3+\delta}$ (LSTO) is an active and redox-stable material and has been considered as the breakthrough in redox-stable anode material for high-temperature solid oxide fuel cell field. The n-type conduction mechanism of LSTO would well fit the strong reducing condition in the cathode and promise better electrode performances than LSCM [10,13]. The LSTO has proven to be an alternative electrode material for direct steam electrolysis in our previous work [24]. Moreover, the A-site deficiency in LSTO, e.g. $La_{0.4}Sr_{0.4}TiO_3$, contributes to an increased electronic conductivity under reducing conditions. The applied potential is expected to electrochemically reduce the LSTO electrode and improve the electrocatalytic and electrical performance of the electrode. However, the electrode performances and Faradic efficiencies for steam electrolysis are still a challenge because of the insufficient catalytic activity of ceramic materials compared to the traditional electrode based on Ni metal.

In this work, perovskite-type $(La_{0.2}Sr_{0.8})_{0.9}Ti_{0.9}Cu_{0.1}O_{3-\delta}$ with A-site deficiency and B-site excess was designed to anchor copper nanoparticles on the $La_{0.2}Sr_{0.8}TiO_{3+\delta}$ surface through a reversible exsolution of copper nanoparticles via a treatment in a high-temperature reducing atmosphere. Electrocatalytic kinetics and high-temperature stability of the copper nanoparticles were expected to be enhanced at the anchored interface. Electrical properties of the reduced LSTO and LSTCO were systematically studied which correlated closely with electrochemical performance of the composite electrodes in symmetrical cells or electrolysis cells. Steam electrolysis performance of LSTO-SDC and LSTCO-SDC cathodes was systematically evaluated in solid oxide electrolyzers with or without reducing gas flowing over the electrodes, respectively.

2.   Experimental

All the powders were purchased from SINOPHARM Chemical Reagent Co. Ltd (China) except specifically stated. The $La_{0.2}Sr_{0.8}TiO_{3+\delta}$ (LSTO) powders were synthesized by the traditional solid-state reaction method [24,25]. Stoichiometric amounts of La_2O_3, $SrCO_3$ and TiO_2 were mixed in acetone and ground in a zirconia ball mill for 10 min. The dried powders were pressed into pellets and sintered at 1400 °C for 10 h in air and then the pellets were ground into yellowish powders. Similarly, the A-site deficiency and B-site excess $(La_{0.2}Sr_{0.8})_{0.9}Ti_{0.9}Cu_{0.1}O_{3-\delta}$ (LSTCO) powders were also prepared by the solid-state reaction method while the heat treatment temperature was 1200 °C 10 h in air. The $(La_{0.8}Sr_{0.2})_{0.95}MnO_{3-\delta}$ (LSM) were synthesized using the above method with the final heat treatment conducted at 1100 °C for 3 h in air [26]; however, the $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ (SDC) powders were prepared by combustion method using Sm_2O_3 and $Ce(NO_3)_4\cdot6H_2O$ precursors and the final treatment temperature was 800 °C for 3 h in air [27–29]. The phase formation of the LSTO, LSTCO, LSM and SDC powders were analyzed by X-ray diffraction (XRD, $2\theta = 3°$ min^{-1}, D/MAX2500V, Rigaku Corporation, Japan).

About 2.0 g of LSTO and LSTCO powders were pressed into bars followed by sintering at 1400 °C for 10 h in air, respectively. The relative density of LSTO and LSTCO reached approximately 83%. The bars of LSTO and LSTCO were reduced at 1200 °C for 5 h in 5%H_2/Ar for conductivity tests, respectively. The conductivity tests were performed in reducing atmosphere (5%H_2/Ar) using DC four-terminal method with temperature ranging from 200 to 800 °C. In this test, the conductivity was recorded versus temperature with an online system at a step 0.5 °C from room temperature to 800 °C. The dependence of conductivity on the oxygen partial pressure was recorded at 800 °C with the oxygen partial pressure ranging from 10^{-20} to 10^{-2} atm. The oxygen partial pressure was adjusted by flowing air at the flow rate of 0.5 ml min^{-1} using mass flow meters. The oxygen partial pressure and conductivity were recorded with an online oxygen sensor (Type 1231, ZrO_2-based oxygen sensor, Noveltech, Australia) and an online multi-meter (Keithley 2000, Digital Multimeter, Keithley Instruments Inc., USA), respectively.

The 2-mm-thick 8YSZ electrolyte support was prepared by dry-pressing the 8YSZ powders into a green disk with a diameter of 20 mm followed by sintering in air at 1500 °C for 10 h [30]. The two surfaces of the YSZ electrolyte support were mechanically polished and ultrasonically cleaned in ethanol and distilled water. The cathode slurries of LSTO-SDC and LSTCO-SDC were prepared by milling the SDC powders with LSTO and LSTCO powders at a 35:65 weight ratio in the alpha-terpineol with appropriate amount of cellulose additives, respectively. The anode slurries of LSM-SDC were prepared by milling LSM powders at a weight ratio 65:35 in the alpha-terpineol with cellulose additives in the same way. The two kinds of electrode slurries were printed onto the electrolyte