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A composite cathode based on scandium-doped chromate for direct high-temperature steam electrolysis in a symmetric solid oxide electrolyzer



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HIGHLIGHTS

- The doping of Sc in LSCM remarkably improves electrode activity.
- Sc doping offers higher oxide-ion conductivity but lower electronic conductivity.
- Promising electrode polarization has been achieved for steam electrolysis.
- Direct steam electrolysis with 100% current efficiency is demonstrated.

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ABSTRACT

Composite cathodes based on $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$ (LSCM) are promising candidates for direct steam electrolysis while their insufficient electro-catalytic activity still restricts Faradic efficiency and electrode performance. In this work, scandium is doped into LSCM (LSCMS) to enhance the performance of the composite cathode. The combined characterization of XRD, TEM, TGA and XPS indicates successful partial replacement of Cr/Mn by scandium in the B site of chromate. The doping of scandium remarkably improves ionic conductivity while accordingly decreases the mixed conductivity. Electrochemical measurements demonstrate the decreased electrode polarizations of LSCMS cathodes. The Faradic efficiencies are accordingly enhanced by 20% and 50% compared with the electrolyzer with LSCM cathode for high temperature steam electrolysis by exposing cathode to 5% $\text{H}_2\text{O}/5\%\text{H}_2/\text{Ar}$ and 5% $\text{H}_2\text{O}/\text{Ar}$, respectively.

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1. Introduction

Solid oxide electrolyzers currently attract a lot of research interests because they provide an alternative to efficiently convert renewable energy to chemical fuel energy [1–5]. Traditional Ni–YSZ composite has been extensively investigated as a cathode materials for steam electrolysis in oxygen ion-conducting solid

oxide electrolyzers [6,7]. However, a certain amount of hydrogen is required to flow over Ni cermet to avoid the oxidation of Ni to NiO, which causes a decrease of electrical conductivity and even the degradation of the electrodes [8,9].

The perovskite $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$ (LSCM) material has been thought as a promising anode of the of solid oxide fuel cell owing to its excellent redox stability, catalytic activity and high durability against sulfur poisoning [10–12]. LSCM is a typical p-type semiconductor with a reasonable conductivity in a large range of oxygen partial pressures. A high SOFC performance is achieved with LSCM anode using 97% $\text{H}_2/3\%\text{H}_2\text{O}$ or CH_4 without excess steam at 900 °C [13,14]. Furthermore, redox-stable LSCM can be employed as a cathode and anode working under oxidizing or reducing

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atmospheres, respectively. The thermal expansion coefficient differences between SOFC/SOE components give rise to significant stress during cell manufacture. Compared to traditional asymmetric SOFCs, the symmetric cells with LSCM electrodes will greatly reduce such stress and indeed enhance the ease of co-sintering, which would significantly reduce manufacture cost [15–19]. The promising performance and long-term stability of LSCM cathode for direct steam electrolysis has been achieved in an oxygen ion-conducting solid oxide electrolyzer even without the presence of reducing gas to protect the cathode. In Irvine's work, solid oxide electrolyzers with LSCM cathodes demonstrate excellent performance for steam electrolysis under external potential load using 3% steam/Ar/4% H_2 and 3% steam/Ar at temperatures between 750 and 1000 °C [20–22]. We have also realized the direct electrolysis of CO_2 to produce CO based on LSCM electrodes in a symmetric oxygen ion-conducting cell. The current efficiency reaches 60–80% at 1.0, 1.5 and 2.0 V at 800 °C [23–25]. However, the limited electro-catalytic activity of LSCM still restricts electrode performance and Faradic current efficiency. To improve electro-catalytic activity, active elements including Fe, Co, Ni, V and Ti are introduced into B site of chromate to modify the perovskite ceramic in previous studies [26–28].

Scandium oxide has been commonly considered as an electro-catalyst and utilized to enhance the electro-catalytic activity of composite electrodes [29–31]. Due to its unique catalytic property, scandium has been widely doped into perovskite electrode materials to improve electrode performance. In Zheng and Shao's work, a significant improvement in electrode performance is attributed to the generation of oxygen vacancies, which are expected to reduce oxygen migration energy at the electrode/electrolyte interface region by the partial reduction of B-site element in perovskite structure, induced by the current polarization [32]. Zhou and Irvine et al. reported the utilization of Sc-doped $(\text{La,Sr})\text{TiO}_{3+\delta}$ as solid oxide fuel cell anode and found that the presence of scandium improves the oxidation and reduction kinetics of composite electrode though the electronic conductivity gradually decreases with doping amount [33,34]. Cheng et al. found that solid oxide fuel cells with LSMS–YSZ cathode showed higher performance than that with LSM–YSZ cathode at low operation temperatures. They believed that the improvements mainly originated from the increase of oxygen vacancies in LSMS, suggesting that the scandium incorporation into LSM brought improved electrochemical activity towards O_2 reduction reaction [35,36].

In this work, scandium is doped into the B site of LSCM to improve the electro-catalytic activity. The crystal structure and oxygen nonstoichiometry of Sc-doped LSCM were studied. The correlation between electrical properties and electrochemical performances was also investigated. Steam electrolysis was performed on Sc-doped LSCM cathode of a symmetric solid oxide electrolyzer with/without the flow of reducing gas over the cathode, respectively.

2. Experimental

All the chemicals (99.9%) were purchased from SINOPHARM Chemical Reagent Co. Ltd (China). The $\text{La}_{0.25}\text{Sr}_{0.75}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$ (LSCM) powders were synthesized by a traditional solid-state reaction method [37,38]. Stoichiometric amounts of La_2O_3 , SrCO_3 , Cr_2O_3 and MnO_2 were mixed in acetone in a zirconia ball mill for 10 min. The dried powders were pressed into pellets and subsequently sintered at 1400 °C for 10 h in air. Then, the pellets were ground into powders. The same procedure was used to prepare B-site substituted $\text{La}_{0.25}\text{Sr}_{0.75}\text{Cr}_{0.5}\text{Mn}_{0.4}\text{Sc}_{0.1}\text{O}_{3-\delta}$ (LSCMS) powder. The $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ (SDC) powders were prepared using a reported procedure and followed by a treatment at 800 °C for

3 h in air [39,40]. The 2-mm-thick YSZ electrolyte supports were fabricated by dry pressing 8YSZ into green disks with a diameter of 20 mm, followed by a heat treatment at 1500 °C for 10 h in air. XRD ($\text{CuK}\alpha$, 3° min^{-1} , $2\theta = 20\text{--}80^\circ$, D/MAX2500V, Rigaku Corporation, Japan) was performed to identify the phase formations of LSCM and LSCMS. X-ray photoelectron spectroscopy (XPS; Al $\text{K}\alpha$, ESCALAB25, Thermo, America) were employed to characterize the materials before and after high temperature reduction in 5% H_2 /Ar at 800 °C for 3 h. High-resolution transmission electron microscopy (HR-TEM, JEM-2100F, JEOL Ltd, Japan) analysis was performed to investigate the microstructures of oxidized and reduced powders. The accelerating voltage is 200 kV and the imaging mode is bright field image. The oxygen nonstoichiometry of the sample was analyzed by a thermogravimetry analysis (TGA) (STA449F3, Naichi Corporation, Germany) at $10^\circ \text{ C min}^{-1}$.

About 2.0 g of LSCM and LSCMS powders were pressed into bars and sintered in air at 1400 °C to obtain samples for mixed conductivity measurements. The conductivities were measured in air or in reducing atmosphere (5% H_2 /Ar) at a temperature step of 0.5 °C using a multi-meter (Keithley 2000, Keithley Instruments, Inc, USA) by a DC four-terminal method with temperature ranging from 300 to 700 °C. The dependence of conductivity on oxygen partial pressure (p_{O_2}) ($0.1\text{--}10^{-20}$ atm) was tested versus oxygen partial pressure, which was recorded using an online oxygen sensor (Type 1231, Noveltech, Australia). Electron-blocking electrode method was used to test ionic conductivity from 400 to 700 °C in air [41–43].

The composite electrode slurry was prepared by mixing SDC powders with LSCM or LSCMS powder at a weight ratio of 35:65 in alpha-terpineol with a proper amount of cellulose additive. The slurry was printed on both surfaces of YSZ discs to assemble symmetric solid oxide cells with a configuration of LSCM–SDC|YSZ|LSCM–SDC or LSCMS–SDC|YSZ|LSCMS–SDC. The two electrode slurries were printed on the electrolyte with an area of approximately 1 cm^2 , followed by a heat treatment at 1100 °C for 3 h in air. Silver paste (SS-8060, Xinluyi, Shanghai, China) was printed on electrode surfaces to form current collectors. The external circuit was made with silver wires (0.4 mm in diameter), which were fastened to current collectors using conductive adhesive (DAD87, Shanghai Research Institute for Synthetic Resins, Shanghai, China), followed by a heat treatment at 550 °C ($3^\circ \text{ C min}^{-1}$) for 30 min in air. Two solid oxide electrolyzers with the configuration of LSCM–SDC|YSZ|LSCM–SDC and LSCMS–SDC|YSZ|LSCMS–SDC were prepared with the above method. The AC impedance spectroscopies of symmetrical cells were measured in different hydrogen partial pressures and different oxygen partial pressures at 700 °C under open circuit voltages (OCV) condition to characterize electrode polarization resistances using an Electrochemical Workstation (IM6, Zahner, Germany; Frequency range: 4 M–0.1 Hz). The oxygen partial pressures and hydrogen partial pressures were controlled by adjusting the ratios of N_2/O_2 and H_2/N_2 using mass flow meters at the total flow rate of 20 ml min^{-1} (D08-3F, Sevenstar, Beijing, China). Scanning electron microscopy (SEM) (20 kV, $\times 1500$, JSM-6490LV, Japan) was employed to observe the cross-sections of symmetric cells. The AC impedance spectroscopy and current–voltage curve ($I\text{--}V$ curve) of the electrolyzers were recorded at the step of 0.004 V s^{-1} . Steam electrolysis was performed in 5% $\text{H}_2\text{O}/5\%\text{H}_2$ /Ar and 5% $\text{H}_2\text{O}/\text{Ar}$ at various applied voltages ranging from 1.2 to 2.0 V at 700 °C. The flow rates of 5% $\text{H}_2\text{O}/5\%\text{H}_2$ /Ar and 5% $\text{H}_2\text{O}/\text{Ar}$ were set at 30 ml min^{-1} using mass flow meters. The output gas from cathode was detected using an online gas chromatograph (GC9790II, Fuli, Zhejiang, China) to analyze hydrogen concentrations.

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