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Efficient CO₂ electrolysis with scandium doped titanate cathode

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ABSTRACT

Perovskite oxide (La,Sr)TiO_{3+δ} (LSTO) cathode has demonstrated promising performance for direct CO₂ electrolysis due to its unique redox-stable properties. However, insufficient electro-catalytic activity of titanate remains a major drawback that limits electrode performance. In this paper, catalytically active scandium is doped to LSTO to enhance cathode performances. The structure, electronic conductivity and ionic conductivity of La_{0.2}Sr_{0.8}Ti_{1-x}Sc_xO_{3+δ} (LSTS_xO) (x = 0, 0.05 and 0.1) are investigated and further correlated with electrode performances. XRD, TEM, TGA and XPS indicate the successful partial replacement of Ti by Sc in the B site of titanate. The improved electrode performances are strongly dependent on scandium doping contents. Promising direct CO₂ electrolysis performance is demonstrated with near 100% current efficiency based on La_{0.2}Sr_{0.8}Ti_{0.9}Sc_{0.1}O_{3+δ} at 1.7 V and 800 °C.

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Introduction

There are growing concerns over the aggravation of global warming and climate change problems, which is caused by the massive CO₂ emissions into atmosphere arising from the production and consumption of fossil fuels [1]. Electrochemical reduction of CO₂ into fuels using renewable electrical energy has been proposed as an alternative for producing renewable fuels as well as reduces CO₂ emissions [2]. Solid-oxide electrolysis cell (SOEC) has been paid a lot of attention because it can directly electrolyze CO₂ into CO using renewable electricity [3,4].

High temperature CO₂ electrolysis has been performed with Ni–YSZ composite cathode in oxide-ion-conducting solid oxide electrolyzers due to its excellent electrochemical behavior and electro-catalytic properties [5]. However, the pre-reduction of the cathode and a certain amount of hydrogen in cathode is required to prevent the oxidation of Ni into NiO. In contrast to Ni–YSZ, perovskite-type (La_{0.75}Sr_{0.25})_{0.95}Cr_{0.5}Mn_{0.5}O₃ (LSCM) has been confirmed as an active and redox-stable electrode material which can be used as both a cathode and anode in solid oxide fuel cells (SOFCs) and high temperature electrolysis [6,7]. The excellent performance and long-term stability of the direct electrolysis of steam or carbon dioxide with LSCM cathode has been

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achieved in oxide-ion-conduction solid oxide electrolyzer even without the reducing gas flowing over cathode. However, insufficient catalytic activity of LSCM cathode limits the electrolysis performance as reported in previous work [8,9]. And the p-type conduction mechanism of LSCM will produce large electrode polarization resistance with strong reducing potential, which inevitably causes chemical and structural changes of cathodes [10].

The redox-stable material $\text{La}_x\text{Sr}_{1-x}\text{TiO}_{3+\delta}$ has been attracted a lot of attention in the field of solid oxide fuel cell [11]. The reduced perovskite $\text{La}_x\text{Sr}_{1-x}\text{TiO}_{3+\delta}$ has n-type conductivity of $\sim 100 \text{ S cm}^{-1}$ in hydrogen at intermediate temperatures [12,13]. The composite cathode based on $\text{La}_x\text{Sr}_{1-x}\text{TiO}_{3+\delta}$ is expected to be able to perform direct electrolysis. And our previous work has proven that titanate cathode delivers stable performances for high temperature electrolysis [12]. It is a pity that the insufficient catalytic activity of such type cathode hinders the electrode performances and Faraday efficiency improvement. As we know, scandium oxide has been commonly utilized to enhance electrocatalytic activity of composite electrodes for its unique catalytic performance. The doping of scandium in the B-site of perovskite $(\text{La,Sr})\text{MnO}_3$ benefits oxygen migration energy in lattice [14]. It is also reported that the $(\text{La,Sr})\text{TiO}_{3+\delta}$ doped with scandium leads to the improvement of the oxidation and reduction kinetics of titanate electrode [15,16]. In other words, the oxygen vacancy linked to Sc improves ionic conductivity and enhance electrode performance.

In this work, scandium is doped to the B-site of $\text{La}_{0.2}\text{Sr}_{0.8}\text{TiO}_{3+\delta}$ to improve the electrocatalytic activity for high temperature CO_2 electrolysis. The crystal structure and oxygen nonstoichiometry of Sc-doped LSTO are studied. The correlation between the conductivity of $\text{La}_{0.2}\text{Sr}_{0.8}\text{Ti}_{1-x}\text{Sc}_x\text{O}_{3+\delta}$ ($x = 0, 0.05$ and 0.1) and electrochemical performances is also investigated. Direct electrolysis of CO_2 with the scandium-doped LSTO cathode is performed in solid oxide electrolyzer at 800°C .

Experimental

The $\text{La}_{0.2}\text{Sr}_{0.8}\text{Ti}_{1-x}\text{Sc}_x\text{O}_{3+\delta}$ ($x = 0$, LSTO; $x = 0.025$, $\text{LSTS}_{0.025}\text{O}$; $x = 0.05$, $\text{LSTS}_{0.05}\text{O}$; $x = 0.075$, $\text{LSTS}_{0.075}\text{O}$; $x = 0.1$, $\text{LSTS}_{0.1}\text{O}$) powders were synthesized by a traditional solid-state reaction method [17]. The solubility limit of Sc in Ti is below 15% in reported work and this is the reason why we chose the Sc concentration up to 10% [14,16]. Stoichiometric amounts of La_2O_3 , SrCO_3 , TiO_2 and Sc_2O_3 were mixed in acetone and ground in a zirconia ball mills for 8 min. The dried powders were pressed into pellets and sintered at 1300°C for 10 h in air and then the pellets were ground into yellowish powders. The $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.95}\text{MnO}_{3-\delta}$ (LSM) were synthesized using the glycine–nitrate combustion method with La_2O_3 , SrCO_3 and $\text{C}_4\text{H}_6\text{MnO}_4 \cdot 4\text{H}_2\text{O}$ and the final heat treatment conducted at 1100°C for 3 h in air [18]. The $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ (SDC) powders were prepared using the above method with stoichiometric amounts of Sm_2O_3 , $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and glycine. And the final heat treatment was conducted at 800°C for 3 h in air [19,20]. Part of the LSTS_xO ($x = 0, 0.025, 0.05, 0.075$ and 0.1) powders were treated in $5\% \text{H}_2/\text{Ar}$ at 1400°C (3°C min^{-1}) for 10 h to reduce the samples. The phase structures of the oxidized and

reduced LSTS_xO ($x = 0, 0.025, 0.05, 0.075$ and 0.1), LSM and SDC powders were analyzed by X-ray diffraction (XRD, $\text{Cu K}\alpha$, $2\theta = 5^\circ \text{ min}^{-1}$, D/MAX2500V, Rigaku Corporation, Japan) ranging from 20 to 80° , and the XRD Rietveld refinement was performed using General Structure Analysis System (GSAS) software [21,22]. Transmission electron microscopy (TEM) analysis was performed to observe the reduced LSTO and $\text{LSTS}_{0.1}\text{O}$ powders; the analysis was performed on a JEOL 2100F field-emission transmission electron microscope operated at 200 kV . X-ray photoelectron spectroscopy (XPS: Al $\text{K}\alpha$, ESCA-LAB250, Thermo, America) was employed to characterize $\text{LSTS}_{0.1}\text{O}$ powders before and after high temperature reduction in $5\% \text{H}_2/\text{Ar}$ at 1400°C for 10 h. Thermogravimetry analysis method (TGA, SDT Q600, America) was used to analyze the oxygen nonstoichiometry of the reduced LSTO and $\text{LSTS}_{0.1}\text{O}$ samples. The microstructure of the LSTO and $\text{LSTS}_{0.1}\text{O}$ was investigated by scanning electron microscopy (SEM, SU8020, HITACHI, Ltd., Japan).

About 1.5 g LSTO, $\text{LSTS}_{0.05}\text{O}$ and $\text{LSTS}_{0.1}\text{O}$ powders were pressed into bars at a pressure of 8 MPa followed by sintering at 1400°C (3°C min^{-1}) for 10 h in air. The bars were reduced at 1400°C for 10 h in $5\% \text{H}_2/\text{Ar}$ for mixed conductivity tests. About 2.0 g LSTO, $\text{LSTS}_{0.05}\text{O}$ and $\text{LSTS}_{0.1}\text{O}$ powders were pressed into pellets followed by treating as well as the mixed conductivity samples for ionic conductivity. The mixed conductivity and ionic conductivity tests were performed in a reducing atmosphere ($5\% \text{H}_2/\text{Ar}$) from 200 to 800°C using a DC four-terminal method with an online multi-meter (Keithley 2000, Digital Multimeter, Keithley Instrument Inc., USA). DC four-terminal method is also known as Van der Pauw measurement, which is widely used to measure the mixed conductivity. For conductivity higher than 1 S cm^{-1} , the data recorded with DC four-terminal method is more accurate. However, samples with ionic conductivity lower than 1 S cm^{-1} can be tested using Hebb-Wagner polarization method [8,21]. The ionic conductivity was tested in $5\% \text{H}_2/\text{Ar}$ using an electron-blocking electrode method which is generally utilized to test ion conductivity for mixed conducting materials and recorded versus temperature using an online system at a step of 1.25°C [23].

Yttria-stabilized zirconia (8YSZ) electrolyte supports with $2 \pm 0.1 \text{ mm}$ in thickness and $20 \pm 0.5 \text{ mm}$ in diameter were prepared by dry-pressing method at 2 MPa , followed by sintering at 1500°C (2°C min^{-1}) for 10 h in air. The $\text{La}_{0.2}\text{Sr}_{0.8}\text{Ti}_{1-x}\text{Sc}_x\text{O}_{3+\delta}$ -SDC ($x = 0, 0.05$ and 0.1) composite electrode slurries were prepared by milling the SDC powders with $\text{La}_{0.2}\text{Sr}_{0.8}\text{Ti}_{1-x}\text{Sc}_x\text{O}_{3+\delta}$ ($x = 0, 0.05$ and 0.1) powders at a 35:65 weight ratio in alpha-terpineol with cellulose as an additive [24]. The SDC has superior ionic conductivity and is expected to deliver oxygen ion transport while the titanate provides electronic conductivity [25–27]. The AC impedance symmetric cells with the configurations of LSTS_xO -SDC|YSZ| LSTS_xO -SDC ($x = 0, 0.025, 0.05, 0.075$ and 0.1) were tested in different hydrogen partial pressures at 800°C , in which frequency is between 4 MHz and 100 mHz at open circuit voltage (OCV). The impedance data was fitted using Zview software to calculate the R_p values. The solid oxide electrolyzers were made with an LSMO anode and a LSTO-SDC, a $\text{LSTS}_{0.05}\text{O}$ -SDC or a $\text{LSTS}_{0.1}\text{O}$ -SDC cathode in the same way as described above. The other detailed preparation process of the

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