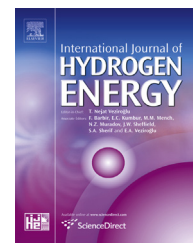




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Catalytic activity of perovskite-type doped $\text{La}_{0.08}\text{Sr}_{0.92}\text{Ti}_{1-x}\text{M}_x\text{O}_{3-\delta}$ ($\text{M} = \text{Mn}, \text{Fe}, \text{and Co}$) oxides for methane oxidation

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ARTICLE INFO

Article history:

Received 10 December 2013

Received in revised form

8 February 2014

Accepted 1 March 2014

Available online 13 April 2014

Keywords:

Methane oxidation

Perovskite oxides

Solid oxide fuel cells

Oxide anodes

Doped strontium titanate

ABSTRACT

Transition metal doped $\text{La}_{0.08}\text{Sr}_{0.92}\text{M}_{0.20}\text{Ti}_{0.80}\text{O}_{3-\delta}$ ($\text{M} = \text{Mn}, \text{Fe}, \text{and Co}$) perovskite oxides were synthesized by the Pechini method. The methane oxidation behavior and the polarization resistance of the solid oxide fuel cells (SOFCs) with the perovskite oxides as anode was subsequently measured as a function of operation temperature. Surface atomic concentrations of the perovskite oxides were evaluated using X-ray photoelectron spectroscopy (XPS) and their relationship to the catalytic activity were discussed with respect to the transition metal dopant. The complete oxidation of methane was predominant in the low-temperature region, while the partial oxidation of methane occurred at high temperatures. Fe- and Co-doped perovskites showed better catalytic activity for the methane oxidation reaction than Mn-doped powder. This phenomenon could be explained by the high atomic concentration with low oxidation states and the resulting high oxygen vacancy concentration in the Fe- and Co-doped perovskite powder samples.

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Introduction

Recently, there has been a growing interest in developing oxide anode materials for direct hydrocarbon solid oxide fuel cells (SOFCs) [1,2]. At the anode, the main reaction is the oxidation of the fuels. Therefore, electronic conductivity, oxygen ionic conductivity, and catalytic activity are very important properties for SOFC anode. Traditionally, a nickel-yttria-stabilized zirconia (Ni-YSZ) cermet has been used for the SOFC anode; however, some problems are evidenced with the use of the Ni-YSZ cermet when hydrocarbons containing

sulfur impurities are used as a fuel. For instance, the effective electrode area reduction by carbon deposition or sulfur poisoning is the most frequently encountered issue [3]. In addition, microstructural changes in the Ni-YSZ anode can occur during the redox cycles [4].

To overcome the above-mentioned limitations of the Ni-YSZ anode, oxide anode materials are being considered as alternative anode materials for SOFCs. Among the potential candidates discussed in the literature, perovskite-type strontium titanates (SrTiO_3), which are doped by rare earth elements, are the most promising candidates for SOFC anodes from the viewpoint of ability to maintain phase stability and

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<http://dx.doi.org/10.1016/j.ijhydene.2014.03.008>

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electronic conductivity under a reducing environment. It is well known that substituting divalent Sr^{2+} with trivalent atoms such as Y^{3+} or La^{3+} can improve the electronic conduction of SrTiO_3 under reduction conditions [5,6]. When transition metals such as Mn, Fe, and Co are replaced in the Ti sub-lattice, both, the oxygen ionic conductivity related to catalytic activity and oxygen vacancy formation, are improved [7,8].

There are some studies investigating the catalytic activity of perovskite-type oxide materials for methane oxidation [9,10]. According to these studies, the catalytic activity depends on the oxidation state of the B-site transition metal elements and oxygen non-stoichiometry that is closely related to oxygen vacancy formation [11,12]. Therefore, it is expected that the catalytic activity of the oxide anode materials can be modified by the partial substitution of strontium and titanium using lanthanum and transition metal elements, respectively.

In this study, 8 mol% of La- and 20 mol% of transition metals such as Mn-, Fe-, or Co-doped SrTiO_3 were synthesized by the Pechini method. Electrolyte supported solid oxide fuel cells with the perovskite oxides as anode were fabricated. The CH_4 conversion rate on the perovskite oxide powders and the polarization resistance of the cell with the perovskite oxide anode were measured as a function of temperature. The effect of surface atomic concentration and oxidation state of the perovskite oxides on the catalytic activity for methane oxidation was also investigated in terms of the surface condition of the B-site dopants.

Experimental procedure

Powder synthesis

Three perovskite-type oxide powders with formulas of $\text{La}_{0.08}\text{Sr}_{0.92}\text{Mn}_{0.20}\text{Ti}_{0.80}\text{O}_{3-\delta}$ (LSMTO), $\text{La}_{0.08}\text{Sr}_{0.92}\text{Fe}_{0.20}\text{Ti}_{0.80}\text{O}_{3-\delta}$ (LSFTO), and $\text{La}_{0.08}\text{Sr}_{0.92}\text{Co}_{0.20}\text{Ti}_{0.80}\text{O}_{3-\delta}$ (LSCTO) were synthesized by the Pechini method. Strontium nitrate (98.0%, Aldrich), lanthanum nitrate (99.0%, Aldrich), titanium isopropoxide (97.0%, Aldrich), cobalt nitrate (99.9%, Junsei), manganese nitrate (99.9%, Kanto Chemical Co., Inc.), iron nitrate (99.9%, Aldrich), citric acid (99.5%, Junsei), and ethylene glycol (99.5%, Junsei) were used as the starting materials. The molar ratio of metal: citric acid: ethylene glycol was 1:2:8. After the titanium isopropoxide was dissolved in ethylene glycol, citric acid and other metal nitrates were added sequentially. The whole process was carried out in a glove box under deactivated nitrogen gas atmosphere. To make a homogeneous precursor, the mixture was stirred and heated on a hot plate at 80 °C for 1 h. Then, the obtained precursor solution was further heated at 120 °C for 8 h to remove the water produced by the polyesterification between ethylene glycol and citric acid. During heating at 120 °C, the solution transformed into a viscous polymeric resin. The resin was dried at 250 °C for 12 h in an oven and was subsequently calcined at 800, 850, and 900 °C for 5 h.

Cell fabrication

The electrochemical performance of the LSMTO, LSFTO, and LSCTO anodes were measured using an electrolyte supported

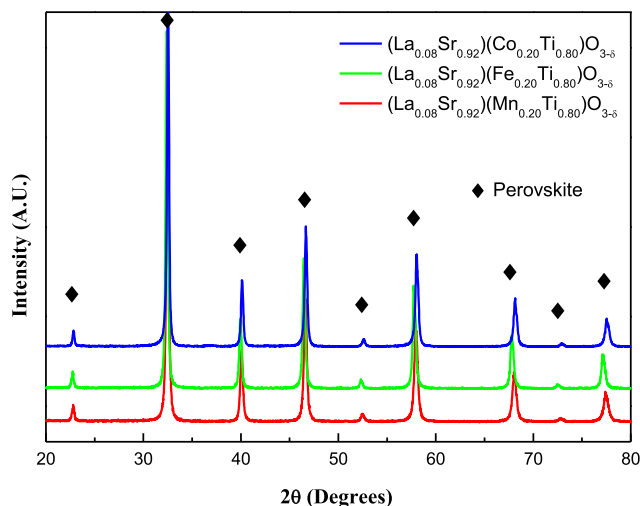


Fig. 1 – XRD patterns of $\text{La}_{0.08}\text{Sr}_{0.92}\text{Mn}_{0.20}\text{Ti}_{0.80}\text{O}_{3-\delta}$ (LSMTO), $\text{La}_{0.08}\text{Sr}_{0.92}\text{Fe}_{0.20}\text{Ti}_{0.80}\text{O}_{3-\delta}$ (LSFTO), and $\text{La}_{0.08}\text{Sr}_{0.92}\text{Co}_{0.20}\text{Ti}_{0.80}\text{O}_{3-\delta}$ (LSCTO) calcined at 800 °C for 5 h in air.

single cells ($\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF)- $\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_2$ (GDC, cathode)/GDC (buffer)/ScSZ (electrolyte)/Anodes). The commercially available ScSZ (89 mol% ZrO_2 -10 mol% Sc_2O_3 -1 mol% Al_2O_3 , Daich Kigenso Kagaku Kogyo Co. Ltd., Japan) powder was pressed into a pellet and sintered at 1500 °C for 5 h in air. A ScSZ disc with a diameter of 20 mm and a thickness of 0.2 mm was obtained. Anode (LSMTO, LSFTO, and LSCTO), LSCF (Fuel Cell Materials, USA)-GDC (gadolinium-doped ceria, Anan Kasei, Japan) cathode, and GDC powders were mixed with an organic vehicle (Fuel Cell Materials, USA) to form pastes. The anode pastes were then applied on the ScSZ electrolyte using screen-printing method, which followed by sintering at 1000 °C for 2 h. The GDC buffer layer was deposited on the opposite side of the ScSZ electrolyte using screen-printing method using a GDC paste, which was then fired at 1400 °C for 2 h in air. Then, the LSCF-GDC was applied on the GDC buffer layer by screen-printing and sintering at 1000 °C for 2 h.

Characterization

For phase characterization, X-ray diffraction (XRD, RU-200B, Rigaku Co. Ltd.) was performed using Ni-filtered $\text{CuK}\alpha$ radiation. The microstructure of the electrode was observed by field emission scanning electron microscopy (FESEM,

Table 1 – BET surface areas of powder samples calcined at 800, 850, and 900 °C, respectively.

BET surface area (m^2/g)	Calcination temperature, °C		
	800	850	900
$(\text{La}_{0.08}\text{Sr}_{0.92})(\text{Mn}_{0.20}\text{Ti}_{0.80})\text{O}_{3-\delta}$	15.96	12.06	6.73
$(\text{La}_{0.08}\text{Sr}_{0.92})(\text{Fe}_{0.20}\text{Ti}_{0.80})\text{O}_{3-\delta}$	14.86	12.33	7.49
$(\text{La}_{0.08}\text{Sr}_{0.92})(\text{Co}_{0.20}\text{Ti}_{0.80})\text{O}_{3-\delta}$	22.44	6.72	2.65

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