

# Ce<sub>0.6</sub>Mn<sub>0.3</sub>Fe<sub>0.1</sub>O<sub>2-δ</sub> as an Alternative Cathode Material for High Temperature Steam Electrolysis Using LaGaO<sub>3</sub>-based Oxide Electrolyte



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## ABSTRACT

Ce<sub>0.6</sub>Mn<sub>0.3</sub>Fe<sub>0.1</sub>O<sub>2-δ</sub> (CMF) has been used as a new oxide cathode of solid oxide electrolysis cell (SOEC) using LaGaO<sub>3</sub>-based electrolyte for H<sub>2</sub> production under a feeding gas composition of 20%steam/1%H<sub>2</sub>/79%Ar. CMF cathode exhibits good electrolysis performance and well-performed hydrogen production rate with the Faraday's law at 1173–973 K. Through impedance measurement under a DC polarized condition, the studies show that polarization resistance and ohmic resistance decreased with increasing DC bias potential. Furthermore, CMF showed good stability, and no significant aggregation and delamination were noticed during the electrolysis measurement. These results suggest that CMF can be a promising oxide cathode candidate for intermediate temperature SOEC.

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## 1. Introduction

Solid oxide fuel cell (SOFC) has been attracting much attention as powerful energy conversion device because of its high energy conversion efficiency and fuel flexibility [1]. Recently, solid oxide electrolysis cell (SOEC), a reversible type of SOFC, provide an efficient way to produce clean hydrogen from high-temperature steam [2–5]. The components of SOEC almost similar with those of SOFC. Therefore, if SOFC and SOEC can be operated in one cell, it would be a potential strategy for energy conversion application between electricity and fuel production (hydrogen in this case), providing an efficient energy storage system [6,7].

Ni-based anode materials, which have been widely used in the conventional SOFC, are also adopted as cathode materials in SOEC due to their good catalytic property and high electronic conductivity. However, Ni-based cathodes have low stability in high pO<sub>2</sub> atmosphere under an electrolysis operating condition of repeated redox cycles, resulting in occurrence of delamination and aggregation [8]. In addition, the Ni-based electrodes are required to be operated with a small amount of H<sub>2</sub> to avoid oxidation, while this leads to a long pre-operation process. To deal with the issues, oxide cathodes have been investigated recently instead of Ni-based materials [9–14] due to good stability for redox cycles and no

need of the H<sub>2</sub> flow for reduction. However, there are several limitations of oxide materials, such as low catalytic property and low electric conductivity, which can not only lead to low electrolysis performance and limit the development of oxide electrode in SOEC. Therefore, a oxide cathode material with appropriate electric conductivity and catalytic property is highly required.

In previous work, a mixed conducting oxide, Mn- and Fe-doped CeO<sub>2</sub> (Ce<sub>0.6</sub>Mn<sub>0.3</sub>Fe<sub>0.1</sub>O<sub>2-δ</sub>, CMF), has been reported as a new oxide anode for SOFC [15]. The catalytic activity of CMF for electrode reaction was reasonably high for SOFC anode application, although its electrical conductivity is lower than that of typical perovskites oxide electrode materials (10<sup>-1</sup> S/cm at 1173 K) [16]. In addition, this material has n-type conduction under reducing atmosphere [17]. Thus, its slightly low electric conductivity is expected to be increased when it is used for SOEC; its electronic conductivity can be increased by the electrochemical reduction under the steam electrolysis condition. In this work, we further investigated the cathode performance of CMF SOEC in comparison with the property of the conventional Ni-based cathodes.

## 2. Experimental

Ce<sub>0.6</sub>Mn<sub>0.3</sub>Fe<sub>0.1</sub>O<sub>2-δ</sub> (CMF) cathode powder was prepared by the following method; Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, Mn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O were dissolved into deionized water. After drying the nitrate solution under a constant stirring, the resultant was

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precalcined in a ventilated decomposition furnace at 673 K for 2 h to remove the nitrogen oxides ( $\text{NO}_x$ ) completely, and was calcined in a furnace at 1273 K for 6 h.  $\text{Ba}_{0.6}\text{La}_{0.4}\text{CoO}_{3-\delta}$  (BLC) anode powder was prepared by a conventional solid-state reaction method. The stoichiometric amounts of  $\text{BaCO}_3$ ,  $\text{La}_2\text{O}_3$ , and  $\text{Co}_3\text{O}_4$  were manually mixed using an  $\text{Al}_2\text{O}_3$  mortar and pestle, followed by a precalcination at 1173 K for 3 h. The precalcined powder was held for a manually intermediate grinding, then following a calcination process at 1473 K for 6 h.

$\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$  (LSGM) electrolyte was also prepared by a solid-state reaction [18]. The stoichiometric amounts of  $\text{La}_2\text{O}_3$ ,  $\text{SrCO}_3$ ,  $\text{Ga}_2\text{O}_3$  and  $\text{MgO}$  were mixed by a manual grinding with the  $\text{Al}_2\text{O}_3$  mortar and pestle. The obtained powder mixture was precalcined at 1173 K for 6 h and then isostatically pressed into disk (2.0 cm in diameter) at 275 MPa for 30 min. The disk was sintered at 1773 K for 6 h in static air and polished down to a thickness of 300  $\mu\text{m}$ .

CMF and BLC were screen-printed on each face of the obtained LSGM disk and calcined at 1373 K for 1 h (effective electrode area: approximately 0.2  $\text{cm}^2$ ). Platinum electrode was used as reference electrode and set close to the anode. For comparison, Ni- $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$  (SDC) (Ni-SDC: 60–40 wt%) cathode cell was also prepared. Thus, two sets of cell configurations of CMF/LSGM/BLC (denoted as cell-A) and Ni-SDC/LSGM/BLC (cell-B) were prepared for the investigation in this work.

Steam electrolysis performance of the cells was measured by a four-probe method in a single-cell testing setup, which has been reported previously [19]. The surface of both cathode and anode was covered with Pt mesh as a current collector. In the case of cell-A using CMF as a cathode, a better contact with the Pt mesh is required due to low conductivity of CMF oxide, as mentioned previously. Thus, to address this problem, Pt mesh current collector was put into the cathode layer by the following approach. After the screen printing of CMF ink, the Pt mesh was embedded into the top of the electrode before drying the ink, followed by calcination at 1373 K for 1 h. By this approach, the prepared CMF electrode can have a well-contact with the Pt current collector. Steam with 1%  $\text{H}_2$  and Ar (steam: $\text{H}_2$ :Ar = 20:1:79 vol%) was fed to the cathode side and a sweep gas of air to the anode side; the total gas flow rate was constantly kept to 100 ml/min in both sides.

On the other hand, a Ni/SDC composite was used as a cathode in cell-B, and reduced by a constant  $\text{H}_2$  flow at 1173 K before electrolysis operation. During the electrolysis measurements, a

feeding composition of steam with 1%  $\text{H}_2$  and Ar (steam: $\text{H}_2$ :Ar = 20:1:79 vol%) was fed at cathode side and air at anode side as a sweep gas. The total gas flow rate at both sides of the cell was kept at 100 ml/min. The cell testing was operated by a galvanostat (HAL-3001, Hokuto Denko Corp.) and the terminal voltage was measured using a digital multimeter (R6451A, Advantest Corp.).

Steam was generated in an evaporation chamber where water was supplied by a micropump (LC-20AT, Shimadzu Corp.). The formation rate of  $\text{H}_2$  was analyzed using gas chromatograph (GC) with a thermal conductive detector (GC-8A, Shimadzu Corp.). The  $\text{H}_2$  production was measured three times at each operated current in order to minimize the experimental error. Impedance spectrum analysis was characterized using the impedance/gain-phase analyzer (Solartron type 1260, Solartron Co., Ltd.) combined with the electrochemical interface (Solartron type 1287, Solartron Co., Ltd.). Furthermore, a long-term stability of CMF cathode was measured over 90 h at 275  $\text{mA}/\text{cm}^2$  under a feeding gas composition of 20%steam/80%Ar gas at 1073 K. After the electrochemical measurements, the phase stability of the tested cell was conducted by X-ray diffraction (XRD) analysis and scanning electron microscope (SEM) observation. The crystal structure of CMF was identified by XRD (RINT2500, Rigaku). The microstructures of cathode and cross-section images of cathode/electrolyte were characterized by field emission scanning electron microscope (FE-SEM, Versa 3D, FEI).

Long-term stability measurements?

### 3. Results and discussions

Fig. 1 shows the I–V curves of CMF/LSGM/BLC (cell-A) and Ni-SDC/LSGM/BLC (cell-B) measured from 1173 K to 973 K under a gas composition of 20%steam/1% $\text{H}_2$ /79%Ar. As shown in Fig. 1, the current densities of the cell-A was reached to 1.50, 0.61, 0.21  $\text{A}/\text{cm}^2$  at 1.5 V at 1173, 1073, 973 K, respectively. Compared to the cell-B, cell-A shows the slightly lower performance but this performance is also considerable. In general, using oxides as fuel electrodes in either SOFC or SOEC shows considerably lower performance than Ni based electrodes. However, the CMF oxide cathode presents good electrochemical performance, which suggests that CMF is highly active for steam electrolysis and can be suitable in the SOEC operation.

Hydrogen formation rates of the cell-A is demonstrated in Fig. 2 and plotted as a function of current density from 1173 to 973 K. The

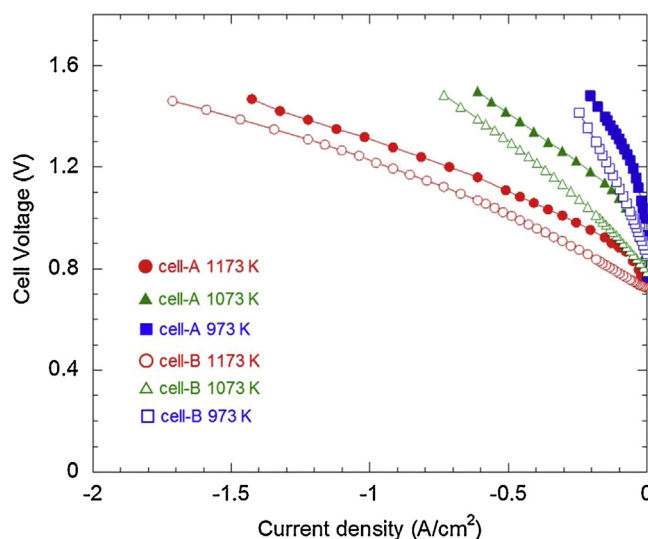


Fig. 1. I–V curves at respective temperatures for the cell-A and cell-B under an atmosphere of 20%steam/1% $\text{H}_2$ /79%Ar.

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