



# Manganese-doped lanthanum calcium titanate as an interconnect for flat-tubular solid oxide fuel cells



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## HIGHLIGHTS

- Manganese and lanthanum doped calcium titanate is synthesized and characterized.
- The highest electrical conductivity is 12.2 and 2.7 S cm<sup>-1</sup> in H<sub>2</sub> and air respectively.
- A cost effective screen-printing is developed to fabricate a dense interconnect layer.
- The maximum power density of co-sintered flat tubular cell is 207.94 mW cm<sup>-2</sup> at 800 °C.
- Area specific resistance of anode supported cell is 1.23 Ω cm<sup>2</sup> at 800 °C.

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## ABSTRACT

A cost-effective screen-printing process is developed to fabricate a dense layer of solid oxide fuel cell (SOFC) interconnect material. A series of lanthanum–manganese-doped CaTiO<sub>3</sub> perovskite oxides (La<sub>0.4</sub>Ca<sub>0.6</sub>Ti<sub>1-x</sub>Mn<sub>x</sub>O<sub>3-δ</sub>; (x = 0.0, 0.2, 0.4, 0.6)) powders is successfully synthesized using an EDTA-citrate method and co-sintered as an interconnect material on an extruded porous anode substrate in a flat-tubular solid oxide fuel cell. All samples adopt a single perovskite phase after calcination at 950 °C for 5 h. High-temperature XRD confirms that the perovskite structure is thermally stable in both oxidizing and reducing conditions. The highest electrical conductivity occurs when x = 0.6; at 12.20 S cm<sup>-1</sup> and 2.70 S cm<sup>-1</sup> under oxidizing and reducing conditions. The thermal expansion coefficient of La<sub>0.4</sub>Ca<sub>0.6</sub>Ti<sub>0.4</sub>Mn<sub>0.6</sub>O<sub>3</sub> is 10.76 × 10<sup>-6</sup> K<sup>-1</sup>, which closely matches that of 8 mol% yttria-stabilized zirconia. Chemical compatibility of samples and their reduction stability are verified at the operating temperature. The power density and area-specific resistance value at x = 0.6 is 208 mW cm<sup>-2</sup> and 1.23 Ω cm<sup>2</sup> at 800 °C under open circuit voltage, and 200 mV signal amplitude under 3% humidified hydrogen and air respectively. This performance indicates that La<sub>0.4</sub>Ca<sub>0.6</sub>Ti<sub>0.4</sub>Mn<sub>0.6</sub>O<sub>3-δ</sub> has potential for use as interconnect in a flat tubular SOFC.

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## 1. Introduction

Solid oxide fuel cells (SOFCs) are electrical power generators which have high power density and efficiency; they are environmentally benign due to their relatively low emission of pollutants [1,2]. SOFCs are usually designed as a series of stacks by applying an interconnect (IC) which provides a path for electricity to flow from the anode of one cell to the cathode of the adjacent one, and also excludes the fuel gas from the oxidant [3,4].

For SOFCs to be commercially viable a reliable and inexpensive IC material is required; it must have good electrical conductivity with low ohmic loss, reasonable thermal conductivity, adequate chemical and mechanical stability in both reducing and oxidizing atmospheres, similar coefficients of thermal expansion with other cell components, good sinterability, and sufficient density to prevent gas penetration [1,2].

To commercialize SOFC technology and increase cell performance, a flat-tubular (FT) SOFC has been designed; this is a combination of planar and tubular configurations. FT-SOFCs are easily sealed, tolerant of thermal stress, and have high volumetric power density. The SOFC described in this work is the anode-supported FT-SOFC, which is composed of a porous anode and a thin-coated dense membrane as an IC [5,6].

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The Ceramic material is the only acceptable IC in the FT-SOFC configuration, and an alternative material to the currently-used ceramic IC (La doped-CrO<sub>3</sub>) would be beneficial because of its difficulty in sintering to high density [7].

CaTiO<sub>3</sub> ceramic perovskite has attracted research attention as an appropriate material for the anode and interconnect, because of its ability to accept a variety of rare earth elements (REEs) into the titanate solid solution to make REE<sub>x</sub>Ca<sub>1-x</sub>TiO<sub>3</sub> [8]. La<sup>3+</sup> may be the most interesting REE; it converts CaTiO<sub>3</sub> to a n-type La<sub>x</sub>Ca<sub>1-x</sub>TiO<sub>3</sub> semiconductor [9,10].

LaCaTiO<sub>3+δ</sub> is well-known for its stability under a wide range of oxygen partial pressure (pO<sub>2</sub>) and for high electrical conductivity, under reducing atmosphere at elevated temperature [11]. At high temperature, A-site deficient La<sub>1-x</sub>Ca<sub>x</sub>TiO<sub>3</sub> and La<sub>2(1-x)/3</sub>Ca<sub>x</sub>TiO<sub>3</sub> perovskites are n-type semiconductor ceramic oxides over a wide range of pO<sub>2</sub> from 10<sup>-15</sup> to 10<sup>5</sup> atm [12]. Lanthanum-doped SrTiO<sub>3</sub> (LST) has been realized as an IC material in contact with fuel gas [13], with a dense Sr<sub>0.7</sub>La<sub>0.2</sub>TiO<sub>3</sub> coated on the anode side [5]. Although LST has high electrical conductivity in a reducing environment, and is therefore suitable for use as an IC material, it undergoes phase transformation with slow redox kinetics in an oxidizing atmosphere [14]. In LST with n-type semiconducting behavior, the electrical conductivity increases after it is reduced at elevated temperature [15]. To increase the electrical conductivity and stability of LST, one suggested method is to dope it on the B-site with transitional metals (TMs) [16,17]. Partial replacement of Ti with Mn leads to a new group of lanthanum–manganese-doped SrTiO<sub>3</sub> perovskite oxides (LSTM) with reasonable thermal expansion, and good electrochemical activity [18,19]. Calcium has been introduced as a substitute for Sr to make LCTM perovskite oxides and different compositions has been synthesized and characterized in terms of crystal structure, thermal expansion, and transport properties (e.g., Ca<sub>0.67</sub>La<sub>0.33</sub>Mn<sub>0.33</sub>Ti<sub>0.67</sub>O<sub>3</sub>, La<sub>0.1</sub>Ca<sub>0.9</sub>Mn<sub>1-x</sub>Ti<sub>x</sub>O<sub>3</sub>, and La<sub>0.5</sub>Ca<sub>0.5</sub>Mn<sub>0.5</sub>Ti<sub>0.5</sub>O<sub>3</sub>) [11,20,21]. However, until now, systematic investigation of Mn substitution effect on La doped calcium titanates under both oxidizing and reducing conditions has not been done. The current work has been conducted to evaluate the feasibility of using LCTM for construction of ICs in FT-SOFC stacks. In this work, we undertake a detailed study of the crystal structure, microstructure, sintering behavior, thermal expansion, electrical conductivity, reduction stability, and polarization behavior to show that the compound is a potential candidate for use as a dense IC film on an anode-supported SOFC.

## 2. Experimental

### 2.1. Preparation of interconnect powder

A series of La<sub>0.4</sub>Ca<sub>0.6</sub>Ti<sub>(1-x)</sub>Mn<sub>x</sub>O<sub>3-δ</sub> (x = 0.0, 0.2, 0.4, 0.6) perovskite powders (hereafter abbreviated as LCTMx, 0 ≤ x ≤ 0.6) was

prepared using a modified EDTA-citrate method [22]. Calculated amounts of La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (99%, Aldrich), Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (98.50%, Aldrich), Mn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (98%, Aldrich) and Ti(OCH(CH<sub>3</sub>)<sub>2</sub>)<sub>4</sub> (97%, Aldrich) solution in ethanol (97%, Aldrich), were dissolved in EDTA (99.9%, Aldrich)–NH<sub>4</sub>OH (28%, Daejung) buffer solution. The molar ratio of EDTA:total metal ion:citric acid was held at 1:1:1.5 under constant stirring.

The mixture was heated to 80 °C; a gel resulted, which was then dried at 150 °C overnight in an oven in air to yield a black powder. To remove all carbon remnants, the powder was pre-calcined at 700 °C for 1 h. The resulting powder was homogenized by ball-milling with zirconia balls for 12 h. The fine reactive LCTMx powders produced by grinding were then calcined at 950 °C for 5 h. Alpha-terpinol (Aldrich) and ethyl cellulose (Aldrich) were mixed in a ratio of 90:10 w:w and then stirred for 24 h at 80 °C as a paste for IC screen printing.

### 2.2. Flat tubular cell fabrication

The anode support was fabricated by extrusion of a mixture of NiO (JT Baker) and 8 mol% Y<sub>2</sub>O<sub>3</sub>-stabilized zirconia (YSZ) (Tosho) in a ratio of 55:45 w:w which had previously been ball milled at 80 rpm for 4 days. After drying at 80 °C for 24 h the mixture was fired at 900 °C for 6 h. Polyvinyl butyral (PVB) as an organic binder, and 10 wt% graphite (Aldrich) as a pore former, were added to the NiO–YSZ mixture and it was allowed to age for 1 day, followed by a repeat of the mixing and firing processes. The mixture was then extruded through a die, using an extruder (KSM 5A, Electro Chuk-Master). The resultant flat tube was 280 mm long, 28 mm wide, 5 mm thick and included five rectangular holes (Fig. 1).

This extruded anode support was pre-sintered at 1200 °C for 3 h, then dipped into a slurry of anode functional layer (AFL) with the same components such that the ratio of NiO:YSZ was kept at 55:45 w:w, and sintered in air at 900 °C for 3 h. The obtained thickness of the AFL was 10 μm. A rectangular area of anode support (2 × 16 cm = 32 cm<sup>2</sup>) on one side was masked for interconnect coating, and YSZ slurry was dip-coated as an electrolyte and sintered at 900 °C for 3 h to achieve a thickness of 15.9 μm. The synthesized LCTMx was milled using an attrition mill (KMDC-0.5B) for 6 h, sieved through a 325-μm mesh then mixed with Alpha-terpinol/ethyl cellulose paste using a mortar and pestle. The dense LCTMx powder was coated as a 20-μm thin film on the YSZ-uncoated area of anode support using screen-printing. The anode support, AFL and IC were co-fired at 1400 °C for 3 h to obtain a half-cell. The full cell was obtained by forming two cathode layers of (La<sub>0.85</sub>Sr<sub>0.15</sub>)<sub>0.9</sub>MnO<sub>3</sub>–YSZ composite (LSM–YSZ) and (La<sub>0.85</sub>Sr<sub>0.15</sub>)<sub>0.9</sub>MnO<sub>3</sub> (LSM) on the other side of the anode support using spray-gun coating and sintering at 1200 °C for 3 h. Finally, a spray-gun was used to coat slurry of La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3</sub> (LSCF) on the sintered cathode layers as a

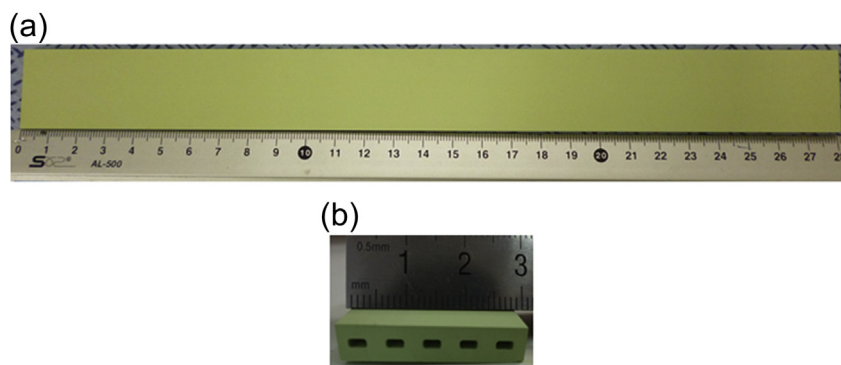


Fig. 1. (a) Photograph of fabricated flat tubular anode support, and (b) Cross section of the extruded anode support.

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