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# Electrophoretic fabrication of *a-b* plane oriented $\text{La}_2\text{NiO}_4$ cathode onto electrolyte in strong magnetic field for low-temperature operating solid oxide fuel cell

Motohide Matsuda<sup>a,\*</sup>, Miwa Hashimoto<sup>a</sup>, Chika Matsunaga<sup>a,b</sup>, Tohru S. Suzuki<sup>b</sup>, Yoshio Sakka<sup>b</sup>, Tetsuo Uchikoshi<sup>b</sup><sup>a</sup> Graduate School of Science and Technology, Kumamoto University, 2-39-1 Kurokami, Kumamoto 860-8555, Japan<sup>b</sup> Fine Particles Engineering Group, Materials Processing Unit, National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

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## ABSTRACT

An oriented  $\text{La}_2\text{NiO}_4$  cathode was successfully fabricated on a dense  $\text{Gd}_2\text{O}_3$ -doped  $\text{CeO}_2$  electrolyte pre-coated with conducting polypyrrole by electrophoretic deposition in a static magnetic field of 12 T for use in low-temperature operating solid oxide fuel cell. The orientation of  $\text{La}_2\text{NiO}_4$  was based on an anisotropic magnetic property in its crystal structure. Firm adhesion of the  $\text{La}_2\text{NiO}_4$  cathode to an electrolyte was made by the co-deposition of starch added as a pore former. The  $\text{La}_2\text{NiO}_4$  cathode with the preferential orientation of the *a-b* plane perpendicular to the surface of the electrolyte showed a polarization loss lower than that with a random orientation, leading to an enhancement in the cell performance at 500 °C.

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## 1. Introduction

A recent trend in the development of solid oxide fuel cell (SOFC) with high energy conversion efficiency is to lower the operating temperature below around 600 °C with the objective of using metallic interconnectors. One of key technologies of SOFCs for low temperature operation is to develop a high performance cathode [1], because cell performances at lower temperatures are considerably limited by the electrode properties at the cathode where reduction of the oxygen by electrons followed by migration of the oxide ions to the electrolyte occurs. Recently, much attention has been focused on the  $\text{K}_2\text{NiF}_4$ -type Ni-based compounds,  $\text{Ln}_2\text{NiO}_4$  ( $\text{Ln} = \text{La}, \text{Pr}$  and  $\text{Nd}$ ) with the excellent mixed conduction of oxide ions and electrons for cathodes applicable for a low-temperature operating SOFC (LT-SOFC) [2–10]. According to a report by Skinner et al. [11], the oxygen diffusivity of  $\text{La}_2\text{NiO}_4$  is much higher than that of  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$  which has been well-studied as an effective cathode. The conduction properties of  $\text{Ln}_2\text{NiO}_4$  were, however, anisotropic due to the layered structure in which  $\text{LnNiO}_3$  perovskite layers are alternatively stacked with  $\text{LnO}$  rock-salt layer along the

*c*-axis direction. A much higher diffusivity of oxide ions has been observed in the *a-b* plane. Therefore, the *a-b* plane orientation to the electrolyte would be beneficial for high performance of the  $\text{Ln}_2\text{NiO}_4$  cathode. Yamada et al. recently succeeded in fabricating a (110) oriented  $\text{Nd}_2\text{NiO}_4$  epitaxial film with an ca. 14 nm thickness on a  $\text{Y}_2\text{O}_3$ -stabilized  $\text{ZrO}_2$  (YSZ) electrolyte, demonstrating the effectiveness of the oriented  $\text{Ln}_2\text{NiO}_4$  cathode for the SOFC [12]. This successful work was undertaken only on the (100) flat surface of the YSZ single crystal using a pulsed laser deposition technique. Recently, a unique process using a magnetic field has been proposed for fabrication of the oriented  $\text{Ln}_2\text{NiO}_4$  cathode [13,14]. The fundamental concept of the magneto-scientific process is based upon the anisotropies of the magnetic properties in asymmetric crystals [15–17]. Murata et al. disclosed from studies of the magnetic orientation behavior of  $\text{Nd}_2\text{NiO}_4$  that the easy-magnetization axis of  $\text{Nd}_2\text{NiO}_4$  is the *c*-axis, and succeeded in fabricating the *a-b* plane perpendicular-oriented  $\text{Nd}_2\text{NiO}_4$  cathode on an electrolyte by droplet-coating of a suspension in a 0.9 T field using neodymium magnets [14].

The authors have applied an electrophoretic deposition (EPD), which is a colloidal process with accumulation of fine powders directly onto substrates in a dc electric field, for SOFC processing [18–22]. Although EPD is a practical process with some technological advantages including simplicity of operation, high deposition

\* Corresponding author.

E-mail address: [mm.2008@alpha.msre.kumamoto-u.ac.jp](mailto:mm.2008@alpha.msre.kumamoto-u.ac.jp) (M. Matsuda).

rates and uniformity of the deposited films even for large and complex forms [23–25], pre-treatments are needed to coat the cathode layer on the electrolyte by EPD, because the electrical conduction of the electrolyte is too low for the EPD. Some groups have succeeded in the EPD of ceramic powders on non-conducting substrates by pre-coating a thin conducting layer before the EPD [26–28]. The pre-coated conducting layers were burned off during heating after the EPD, and the deposited ceramic layers firmly adhered to the non-conducting substrates after the post-heating. In the present study, polypyrrole (Ppy) layers have been pre-coated on Gd<sub>2</sub>O<sub>3</sub>-doped CeO<sub>2</sub> (GDC) electrolytes according to a previous report [27]. This paper shows the electrophoretic fabrication of an oriented La<sub>2</sub>NiO<sub>4</sub> (LNO) cathode on a GDC electrolyte pre-coated with Ppy films in the strong magnetic field of 12 T. In addition, the cathode performance at 500 °C of the *a-b* plane oriented LNO on the GDC is compared to that of the randomly oriented one.

## 2. Experimental procedures

### 2.1. Suspension for EPD

LNO powders were prepared by a conventional solid state reaction using reagent grade chemicals of La<sub>2</sub>O<sub>3</sub> (Nacalai Tesuku Inc., Japan, 99.99%) and NiO (Showa Chem. Ind. Co., Ltd., Japan, 99.9%) as starting materials. Before their use, the La<sub>2</sub>O<sub>3</sub> powder was pre-heated at 900 °C for 2 h in air to remove the surface hydroxide. The mixed powders of La<sub>2</sub>O<sub>3</sub> and NiO was calcined at 800 °C for 10 h in air. A lump of the mixed powders was crushed, then re-mixed, and finally heated at 1400 °C for 4 h in air. The obtained reactant was sufficiently pulverized overnight in ethanol using a ball-mill with zirconia balls in size of 4 mm. X-ray diffraction (XRD) analyses confirmed that the obtained powders were of the single LNO phase. It was observed that most of the LNO particles were pulverized below 1 μm in size by the ball-milling process.

A suspension for the EPD was prepared under the following manner. Butoxyethyl acid phosphate (JP-506H, Johoku Chem. Co., Ltd., Japan), a kind of phosphate ester (PE), and polyethylenimine (PEI) with an average molecular weight of 10,000 (Wako Pure Chem. Ind. Ltd., Japan) were used as dispersants. The PE and PEI were separately dissolved in ethanol to formulate diluted PE and PEI solutions with the concentrations of 10 wt% and 2 wt%, respectively. The PE and PEI solutions were added dropwise to ethanol containing LNO powders in this order until the amount of 2 wt% and 0.12 wt% against the powders, respectively. The “operational pH” monitored using a pH meter calibrated for an aqueous solvent was about 4; however, it must be noted that the real  $p_{aH}$  ( $= -\log a_H$ ), the negative logarithm of the proton activity in a nonaqueous solvent, in the nonaqueous solvent would be different from the monitored value. Rice starch powder (Sigma-Aldrich Co. LLC., product#: S7260, average particle size: 5 μm) was added as a pore former to the suspension obtained was deflocculated using an ultrasonic homogenizer at a frequency of 19.5 kHz and power of 1200 W (Model US-1200, Nihonseiki Kaisha Ltd., Japan) with stirring by magnetic stirrer. The ultrasonication was carried out at room temperature for 10 min before their use.

### 2.2. Pre-coating of Ppy onto GDC electrolyte

Dense electrolytes of 10% Gd<sub>2</sub>O<sub>3</sub>-doped CeO<sub>2</sub> (GDC) were prepared using commercial powder supplied by Anan Kasei Co., Ltd. The GDC powder was compacted into disc-shaped pellets with 20 mm diameter by a uniaxial pressure of 90 MPa, then sintered at 1500 °C for 6 h in air. The surface of the obtained GDC electrolytes was etched for hydrophilization using dc sputtering mode of a plasma coating device (SC-701, Sanyu Electron Co., Ltd., Japan)

without a sputtering target. Before the pre-coating of Ppy, the NiO-GDC anode with 20 μm in thickness was applied to single-side of the 500 μm-thick GDC electrolyte by screen-printing with polyethylene glycol (Kanto Chem. Co., Inc., Japan, an average molecular weight of 400) followed by heating at 1250 °C for 2 h in air, and then the anode and side of the electrolyte were sealed with plastic paraffin films. For pre-coating of the Ppy, 0.01 M ammonium peroxodisulfate as an oxidant and 0.01 M 2,6-naphthalenedisulfonic acid disodium salt as a doping agent were dissolved in distilled water. The partially covered-GDC electrolytes were immersed in the solutions. After cooling of the solutions to 0 °C, 0.01 M pyrrole was added to the cooled solutions with stirring. The electrolytes were left for 12 h in the cooled solutions in which the pyrrole was polymerized into Ppy, and then dried at room temperature in air.

### 2.3. EPD of oriented LNO cathode onto electrolyte in magnetic field

The GDC electrolyte with the Ppy coating was placed in the LNO-dispersed suspension as an electrode for the cathodic EPD, which was carried out at a constant applied voltage using a DC power supply (Source Meter, Model 2400, Keithley Instruments, Inc., USA). A stainless steel plate (ISO No. 4301-304-00-I) was used as the counter electrode, facing the Ppy-coated surface of the GDC electrolyte. A dc electric field was applied between the electrodes with a constant distance of 20 mm. During the EPDs, a static magnetic field was applied using a superconducting magnet, the room temperature bore of which was 100 mm and the maximum strength of the generating magnetic field was 12 T. The deposited layers were heated at 1100 °C for 2 h in air.

The microstructure and thickness of the fabricated LNO cathode were observed by scanning electron microscopy (SEM). XRD with monochromatic Cu-Kα radiation was used to investigate the orientation of the LNO cathodes.

### 2.4. Performance testing of LT-SOFC with oriented LNO cathode

A single cell constructed with the oriented cathode fabricated electrophoretically in a 12 T magnetic field was mounted on the end face of an alumina tube with a 9-mm inner diameter and 13-mm outer diameter in an experimental system using an electric furnace. Pt wire was attached to the edge of the GDC electrolyte as the reference electrode. Measurements of the cell performance were carried out at 500 °C with humidified (3% H<sub>2</sub>O) hydrogen as the fuel and air as the oxidant. The flow rates of the gases were maintained at 50 ml/min. The current across the cell was controlled by a galvanostat, and the terminal voltage was measured by a digital voltmeter.

## 3. Results and discussion

Fig. 1 shows cross-sectional views of the Ppy films coated on the GDC electrolytes with and without the plasma-etching treatment. Continuous Ppy films were firmly adherent to the plasma-etched GDC electrolytes. On the other hand, only a poor Ppy coating was obtained on the GDC electrolytes without the plasma-etching treatment. The coated Ppy films partially peeled off the GDC electrolytes. Thus, the plasma-etching treatment of the GDC substrates effectively improved the homogeneity of the Ppy films for use as an electrode by the EPD process.

Fig. 2 compares the cross-sectional views of the LNO layers electrophoretically deposited on the Ppy film pre-coated GDC electrolytes before and after heating at 1100 °C in air. The EPDs at 50 V were carried out at for 30 min without applying magnetic field. The LNO powders were densely deposited on the Ppy films. The Ppy films between the LNO deposits and GDC electrolytes were

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