



# Fabrication and characterization of oriented Nd<sub>2</sub>NiO<sub>4</sub> bulk and cathode for low-temperature operating solid oxide fuel cell



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## HIGHLIGHTS

- The Nd<sub>2</sub>NiO<sub>4</sub> bulk ceramics were fabricated by slip casting in a 5 T magnetic field.
- The easy-magnetization axis of Nd<sub>2</sub>NiO<sub>4</sub> is the *c*-axis.
- The Nd<sub>2</sub>NiO<sub>4</sub> has the anisotropic electric conductivity and thermal expansion.
- The *a*-*b* planes of the oriented cathodes should be perpendicular to the electrolyte.
- The performance of Nd<sub>2</sub>NiO<sub>4</sub> cathode was improved by the orientation.

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## ABSTRACT

Textured Nd<sub>2</sub>NiO<sub>4</sub> (NNO) bulks were fabricated by slip casting in a 5 T magnetic field generated by a superconducting magnet. The easy-magnetization axis of NNO was determined by X-ray diffraction (XRD) measurements performed on the surfaces parallel and perpendicular to the applied magnetic field direction of the sintered bulk NNO ceramics. The anisotropic electric conductivity and thermal expansion coefficient of the textured NNO were characterized by the conventional DC four-terminal method and dilatometry, respectively. A higher electric conductivity and lower thermal expansion in the direction perpendicular to the *c*-axis were confirmed. Based on the obtained experimental data, fabrication of the *a*-*b* plane perpendicular-oriented NNO cathode layer on a Gd-doped ceria (GDC) electrolyte was finally attempted in a 0.9 T magnetic field generated by neodymium magnets. The effect of the rotation of the magnetic field in the horizontal plane on the orientation condition of the NNO layer was also investigated. The rotation of the magnetic field could produce the random orientation of the *c*-axis while retaining the *a*-*b* plane orientation against the electrolyte. Based on the performance tests of single cells equipped with different oriented NNO cathodes, the ideal situation of the NNO cathode layer leading to good performance is proposed.

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## 1. Introduction

The solid oxide fuel cell (SOFC) is a device that directly converts chemical energy into electrical energy via an electrochemical reaction [1]. SOFCs provide clean, highly efficient energy utilization in wide applications from small stationary power units to larger scale capacities [2,3]. One of the main research subjects in the field of SOFCs is reducing the operating temperature, including the selection of the electrolyte and electrode materials and the optimization

of their microstructures [4–6]. Many investigations on the loss mechanisms by impedance spectroscopy as well as theoretical analyses have revealed that the cathode is the main part for the losses and thus the improvement in electrochemical behavior strongly depends on the selected material and microstructure of the cathode [7–9]. The selection of excellent mixed oxide ionic and electronic conducting materials is a crucial issue. The transport of oxide ions within the electrode materials is advantageous concerning the number of possible reaction pathways [10]. Therefore, high performance electrodes should be composed of either a composite consisting of an electronic and ionic conducting phase or a mixed conducting metal oxide to expand the active reaction area into the electrode volume. Many perovskite-type mixed ionic-

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electronic conductors, such as LaFeO<sub>3</sub> [11], LaCoO<sub>3</sub> [12], La<sub>1-x</sub>Sr<sub>x</sub>CoO<sub>3-δ</sub> (LSC) [13], La<sub>1-x</sub>Sr<sub>x</sub>Fe<sub>1-y</sub>Co<sub>y</sub>O<sub>3-δ</sub> (LSCF) [14] and Ba<sub>1-x</sub>Sr<sub>x</sub>Fe<sub>1-y</sub>Co<sub>y</sub>O<sub>3-δ</sub> (BSCF) [15], have been investigated due to their high catalytic activity for the oxygen reduction reaction as well as a high electric conductivity over a wide temperature range. Their cathode properties have been further improved by increasing the number of triple phase boundaries formed on the electrode-electrolyte interface [16].

Recently, a new family of oxides with the K<sub>2</sub>NiF<sub>4</sub>-type structure has attracted much attention; it has the general formula of A<sub>2</sub>MO<sub>4+δ</sub> (A: alkaline earth or lanthanide, M: transition metal) characterized by some oxygen over-stoichiometry and a mixed valence of M, resulting in a high oxygen bulk diffusion and surface exchange coefficients [17–20]. The intensive studies of Ln<sub>2</sub>NiO<sub>4+δ</sub> (Ln = La, Pr, Nd) compounds have been performed due to the high mobility of the oxygen in these compounds [20]. The structure is made up of sheets of (NiO<sub>6</sub>) octahedral sharing corners interleaved by Ln<sub>2</sub>O<sub>2</sub> layers in which the additional oxygen is localized [21]. The anisotropic crystalline structure makes the Ln<sub>2</sub>NiO<sub>4+δ</sub> a highly-anisotropic electric conductor. It has been revealed that a high oxygen diffusivity [22] and electron transfer [23] occur in the direction parallel to the *a*-*b* plane. These findings strongly suggest that the cell configuration in which the *a*-*b* plane of the Ln<sub>2</sub>NiO<sub>4+δ</sub> cathode is perpendicularly oriented to the electrolyte could produce the best SOFC performance.

Recently, a magnetic field has been applied for fabricating textured non-ferromagnetic ceramics by aligning particles via slurry consolidation [24–26]. The materials used for fabricating the textured structure by utilizing a magnetic field are required to be noncubic or magneto-crystallographically anisotropic. The alignment of a particle with an anisotropic magnetic susceptibility occurs in a magnetic field when the anisotropic magnetic energy of the material is higher than the energy of the thermal motion as follows:

$$\Delta E = \Delta\chi VB^2 / 2\mu_0 > k_B T \quad (1)$$

where  $\Delta E$  is the anisotropic energy,  $\Delta\chi = \chi_{||} - \chi_{\perp}$ ,  $\chi_{||}$  and  $\chi_{\perp}$  are the susceptibilities parallel and perpendicular to the magnetic principal axes, respectively,  $V$  is the volume of the material,  $B$  is the applied magnetic field,  $\mu_0$  is the permeability in a vacuum and  $k_B$  is the Boltzmann constant [25]. The magnetic orientation is likely to be an effective technique for the preparation of crystalline-oriented Ln<sub>2</sub>NiO<sub>4+δ</sub> polycrystalline layers.

In this study, we selected Nd<sub>2</sub>NiO<sub>4+δ</sub> (NNO) among the Ln<sub>2</sub>NiO<sub>4+δ</sub> compounds and attempted to apply the *a*-*b* plane oriented NNO cathode layer on a Gd-doped ceria electrolyte using the magnetic orientation technique. This technique is, however, not applicable without knowing the easy-magnetization axis of NNO. Therefore, we first determined the easy-magnetization axis of NNO. The performance was then evaluated using the single cells with oriented and randomly-oriented NNO cathodes.

## 2. Experimental

### 2.1. Investigation of magnetic orientation behavior of NNO

The NNO powder was synthesized by a solid state reaction. Reagent grade chemicals of Nd<sub>2</sub>O<sub>3</sub> (>99.9%) and NiO (>99.9%) were mixed together with a small amount of ethanol in a mortar, and then calcined in air at 800 °C for 10 h. The calcined powder was ground, then thermally treated in air at 1400 °C for 4 h. The obtained substance was ground into a powder again by ball milling for 48 h and then confirmed to be single-phase NNO by X-ray diffraction (XRD). Scanning electron microscopic observations

showed that most of the particles were less than 1 μm in size after the ball milling. The synthesized NNO powder was dispersed in pure water by ball milling along with adding 1 wt% against the powder of ammonium polycarboxylate (A6114, Toagosei Co., Japan) as a dispersant to formulate the suspension with a 20 vol% solid content. The suspension was ultrasonicated for 10 min while mixed using a magnetic stirrer to ensure the dispersion of the NNO powder. The prepared suspension was defoamed in a vacuum prior to its use for the subsequent slip casting.

The NNO bulks were fabricated by a slip casting technique. During the consolidation of the prepared suspension, a 5 T strong magnetic field was applied parallel to the casting direction. The consolidated cakes were calcined at 500 °C for 1 h in air to remove the dispersant and then sintered at 1400 °C for 4 h for densification. The sintered bulks were cut into cuboids with a diamond saw and then polished with abrasive papers. The specimens were thermally treated in air at 1000 °C for 2 h to homogenize the surface condition. The two orthogonal surfaces, perpendicular and parallel to the direction of the applied magnetic field, of the obtained bulks were characterized by XRD in order to investigate their crystalline-oriented structure. The degree of crystalline orientation was evaluated using the Lotgering orientation factor  $f$  from the intensities of the XRD peaks [27]. The orientation factor  $f(hk0)$  is defined by the following equations:

$$f = (\rho - \rho_0) / (1 - \rho_0) \quad (2)$$

$$\rho = \Sigma I(hk0) / \Sigma I(hkl) \quad (3)$$

$$\rho_0 = \Sigma I_0(hk0) / \Sigma I_0(hkl) \quad (4)$$

where  $I$  and  $I_0$  are the relative intensities of each reflection peak of the (*hkl*) planes;  $\rho$  and  $\rho_0$  are the values calculated from the XRD data measured for the NNO bulks and NNO powder, respectively.

### 2.2. Measurements of electric conductivity and thermal expansion

The total electric conductivities of the NNO bulks were measured by the conventional DC four-terminal method in order to investigate the anisotropy of the electrical property. The total conductivities were measured in the two orthogonal directions, which were parallel and perpendicular to the applied magnetic field direction, at 200–800 °C in air under the applied constant current of 100 mA. The measurements at each temperature were repeatedly carried out until the conductivities became stable.

The linear thermal expansions of the NNO bulks were measured using a dilatometer (TD5000S, Bruker AXS Co., Ltd., Japan) at 30–1000 °C in air to investigate the anisotropy of the thermal expansion. The NNO bulk specimens large enough for the measurement were prepared by slip casting in a 5 T strong magnetic field generated by a superconducting magnet (HF5-100VT-50H-1, Sumitomo Heavy Industries, Ltd., Japan). The sintered samples were cut and polished in the same way as already described.

### 2.3. Fabrication and characterization of single cell with NNO-oriented cathode

Oriented and randomly-oriented NNO cathodes were fabricated on Gd<sub>0.1</sub>Ce<sub>0.9</sub>O<sub>1.95</sub> (GDC) electrolytes in and out of a 0.9 T magnetic field generated by a pair of neodymium magnets, respectively, in order to evaluate the effect of the cathode orientation. The neodymium magnets were placed on a turntable so as to rotate the direction of the magnetic field applied to the NNO suspension which is dropped on a GDC electrolyte suspended at the center

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