

CHAPTER II EXPERIMENTAL

The chemicals and experimental procedures including preparation and characterization of materials are described below:

2.1 Chemicals

The chemicals and reagents listed in Table 2.1 were used without further purification.

Table 2.1 Chemicals and reagents for synthesis of materials

Chemicals and reagents	Formula weight	Purity%	Company
$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	433.02	99.0	Himedia
$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	236.15	99.0	Analytical
$\text{Sr}(\text{NO}_3)_2$	211.63	99.0	Aldrich
$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	290.81	97.0	Ajax
$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	291.03	≥ 98.0	Ajax
$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	404.00	≥ 98.0	Fluka
$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	297.48	99.0	Fluka
La_2O_3	325.79	≥ 99.99	Wako
SrCO_3	147.63	≥ 99.9	Aldrich
Ga_2O_3	187.44	≥ 99.99	Aldrich
MgO	40.3	≥ 98.0	Fluka
NiO	74.60	≥ 99.9	Aldrich
$\text{C}_6\text{H}_8\text{O}_7$	192.43	≥ 99.5	Aldrich
HNO_3	63.01	65	Merck
liq. NH_3	35.05	25	Merck

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2.2 Material preparation

2.2.1 Cathode preparation

Modified citrate method was used for the formation of all cathodes. The abbreviation and composition of the different compounds synthesized are summarized in Table 2.2

Table 2.2 The composition of all prepared cathodes

Composition	Abbreviation
-Substitution La and Sr with Ca in $\text{La}_{1.6}\text{Sr}_{0.4}\text{NiO}_4$	
$\text{La}_{1.6}\text{Sr}_{0.4}\text{NiO}_4$	LSN
$(\text{La}_{0.8}\text{Sr}_{0.2})_{1.9}\text{Ca}_{0.1}\text{NiO}_4$	LSN-Ca _{0.1}
$(\text{La}_{0.8}\text{Sr}_{0.2})_{1.8}\text{Ca}_{0.2}\text{NiO}_4$	LSN-Ca _{0.2}
$(\text{La}_{0.8}\text{Sr}_{0.2})_{1.7}\text{Ca}_{0.3}\text{NiO}_4$	LSN-Ca _{0.3}
$(\text{La}_{0.8}\text{Sr}_{0.2})_{1.6}\text{Ca}_{0.4}\text{NiO}_4$	LSN-Ca _{0.4}
$(\text{La}_{0.8}\text{Sr}_{0.2})_{1.5}\text{Ca}_{0.5}\text{NiO}_4$	LSN-Ca _{0.5}
-Substitution La and Sr with Ca in $\text{La}_{1.6}\text{Sr}_{0.4}\text{Ni}_{0.9}\text{Co}_{0.1}\text{O}_4$	
$\text{La}_{1.6}\text{Sr}_{0.4}\text{Ni}_{0.9}\text{Co}_{0.1}\text{O}_4$	LSNC
$(\text{La}_{0.8}\text{Sr}_{0.2})_{1.9}\text{Ca}_{0.1}\text{Ni}_{0.9}\text{Co}_{0.1}\text{O}_4$	LSNC-Ca _{0.1}
$(\text{La}_{0.8}\text{Sr}_{0.2})_{1.8}\text{Ca}_{0.2}\text{Ni}_{0.9}\text{Co}_{0.1}\text{O}_4$	LSNC-Ca _{0.2}
$(\text{La}_{0.8}\text{Sr}_{0.2})_{1.7}\text{Ca}_{0.3}\text{Ni}_{0.9}\text{Co}_{0.1}\text{O}_4$	LSNC-Ca _{0.3}
$(\text{La}_{0.8}\text{Sr}_{0.2})_{1.6}\text{Ca}_{0.4}\text{Ni}_{0.9}\text{Co}_{0.1}\text{O}_4$	LSNC-Ca _{0.4}
$(\text{La}_{0.8}\text{Sr}_{0.2})_{1.5}\text{Ca}_{0.5}\text{Ni}_{0.9}\text{Co}_{0.1}\text{O}_4$	LSNC-Ca _{0.5}
-Substitution Ni with Fe or Zn in $\text{La}_2\text{Ni}_{0.9}\text{Co}_{0.1}\text{O}_4$	
$\text{La}_2\text{Ni}_{0.9}\text{Co}_{0.1}\text{O}_4$	LNC
$\text{La}_2\text{Ni}_{0.89}\text{Co}_{0.1}\text{Fe}_{0.01}\text{O}_4$	LNC-Fe _{0.01}
$\text{La}_2\text{Ni}_{0.87}\text{Co}_{0.1}\text{Fe}_{0.03}\text{O}_4$	LNC-Fe _{0.03}
$\text{La}_2\text{Ni}_{0.85}\text{Co}_{0.1}\text{Fe}_{0.05}\text{O}_4$	LNC-Fe _{0.05}
$\text{La}_2\text{Ni}_{0.8}\text{Co}_{0.1}\text{Fe}_{0.1}\text{O}_4$	LNC-Fe _{0.1}
$\text{La}_2\text{Ni}_{0.7}\text{Co}_{0.1}\text{Fe}_{0.2}\text{O}_4$	LNC-Fe _{0.2}



$\text{La}_2\text{Ni}_{0.89}\text{Co}_{0.1}\text{Zn}_{0.01}\text{O}_4$	LNC-Zn _{0.01}
$\text{La}_2\text{Ni}_{0.87}\text{Co}_{0.1}\text{Zn}_{0.03}\text{O}_4$	LNC-Zn _{0.03}
$\text{La}_2\text{Ni}_{0.85}\text{Co}_{0.1}\text{Zn}_{0.05}\text{O}_4$	LNC-Zn _{0.05}
$\text{La}_2\text{Ni}_{0.8}\text{Co}_{0.1}\text{Zn}_{0.1}\text{O}_4$	LNC-Zn _{0.1}
$\text{La}_2\text{Ni}_{0.7}\text{Co}_{0.1}\text{Zn}_{0.2}\text{O}_4$	LNC-Zn _{0.2}
-Substitution La with Ca in $\text{La}_2\text{Ni}_{0.85}\text{Co}_{0.1}\text{Fe}_{0.05}\text{O}_4$	
$\text{La}_2\text{Ni}_{0.85}\text{Co}_{0.1}\text{Fe}_{0.05}\text{O}_4$	LNCF
$\text{La}_{1.9}\text{Ca}_{0.1}\text{Ni}_{0.85}\text{Co}_{0.1}\text{Fe}_{0.05}\text{O}_4$	LNCF -Ca _{0.1}
$\text{La}_{1.7}\text{Ca}_{0.3}\text{Ni}_{0.85}\text{Co}_{0.1}\text{Fe}_{0.05}\text{O}_4$	LNCF -Ca _{0.3}
$\text{La}_{1.5}\text{Ca}_{0.5}\text{Ni}_{0.85}\text{Co}_{0.1}\text{Fe}_{0.05}\text{O}_4$	LNCF -Ca _{0.5}
$\text{La}_{1.3}\text{Ca}_{0.7}\text{Ni}_{0.85}\text{Co}_{0.1}\text{Fe}_{0.05}\text{O}_4$	LNCF -Ca _{0.7}
-Substitution La with Ca in $\text{La}_2\text{Ni}_{0.85}\text{Co}_{0.1}\text{Zn}_{0.05}\text{O}_4$	
$\text{La}_2\text{Ni}_{0.85}\text{Co}_{0.1}\text{Zn}_{0.05}\text{O}_4$	LNCZ
$\text{La}_{1.9}\text{Ca}_{0.1}\text{Ni}_{0.85}\text{Co}_{0.1}\text{Zn}_{0.05}\text{O}_4$	LNCZ -Ca _{0.1}
$\text{La}_{1.7}\text{Ca}_{0.3}\text{Ni}_{0.85}\text{Co}_{0.1}\text{Zn}_{0.05}\text{O}_4$	LNCZ -Ca _{0.3}
$\text{La}_{1.5}\text{Ca}_{0.5}\text{Ni}_{0.85}\text{Co}_{0.1}\text{Zn}_{0.05}\text{O}_4$	LNCZ -Ca _{0.5}
$\text{La}_{1.3}\text{Ca}_{0.7}\text{Ni}_{0.85}\text{Co}_{0.1}\text{Zn}_{0.05}\text{O}_4$	LNCZ -Ca _{0.7}

- Preparation of powder

Stoichiometric amounts of corresponding metal nitrates were dissolved in deionized water and nitric acid. Subsequently, citric acid in the molar ratio of 2 mol of citric acid to 1 mol of metal ions was added drop wise into the solution with continuous stirring at room temperature. After 3 hours, ammonia solution was slowly added to adjust the pH value of the solution to about 9 and then stirred at room temperature for 2 hours. The obtained solution was dehydrated and slowly heated until self-combustion of the precipitate. The resulting ash was then ground using a mortar pestle and finally calcined at 900°C for 10 hours in an air-muffle furnace.

- Preparation of disc

The calcined powders were finely ground with ethanol by a mortar pestle for 30 minutes. The 1.8 g fine powders were loaded into the cavity of a KBr die to

prepare a round disc (20 mm in diameter). The die having metal oxide powder inside was knocked against table for 2-3 times to evaporate air inside the powder. After the die was completely assembled, the plunger was brought to the surface of the powders gently for final leveling and smoothing surface. After that the pressure was slowly applied about 2 tons for 10 minutes to obtain a disc. Then the disc was sintered at 1350°C for 10 hours in air.

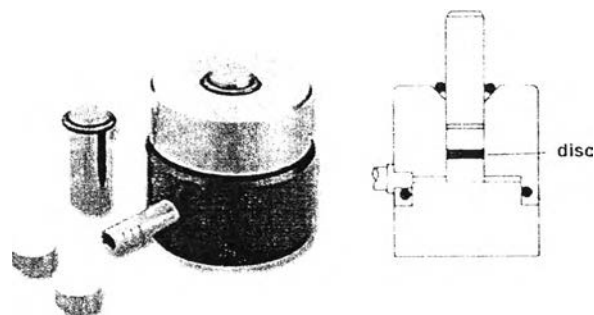


Figure 2.1 KBr die assembly

2.2.2 Anode preparation [36]

The anode used was NiO-Fe₂O₃ (9:1), which synthesized by conventional impregnation technique. Fe(NO₃)₃·9H₂O was firstly dissolved in DI water, followed by the addition of NiO. After that the mixed solution was evaporated and finally the brown powder resulted. The obtained powder was calcined in a furnace at 400°C for 2 hours to get rid of the remaining nitrate and then fired at 1200°C for 6 hours. In order to obtain a fine and uniform particle mixture, the resulting powder was ground in ethanol for 1 hour.

2.2.3 Electrolyte preparation [37]

La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O₃ (abbreviated as LSGM) was used as electrolyte in this study. It was synthesized by conventional solid state method. Calculated amounts of La₂O₃, SrCO₃, Ga₂O₃ and MgO were mixed for 1 hour in a mortar pestle and then calcined at 1000°C for 6 hours. The resulting powders were pulverized and pressed isostatically into a disc (20 mm in diameter). The discs were sintered at 1500°C for 5 hours in air and then polished to the thickness of 0.3 mm by a diamond grinding machine.

2.3 Material characterization

2.3.1 X-ray diffractometry (XRD)

The phase formation of the sintered samples was examined by X-ray powder diffraction using a Rigaku Dmax-2200 Ultima⁺ diffractometer with monochromatic Cu K α radiation (40 kV, 30 mA) at Department of Chemistry, Faculty of Science, Chulalongkorn University. The data was collected in the range of 20 to 70 degree with scan speed of 5 degree/min and the lattice parameter were calculated based on the XRD data with Jade software.

2.3.2 Scanning electron microscopy (SEM)

Microstructural characterization of the sample discs was carried out with a JEOL JSM-5800LV scanning electron microscopy with an Oxford Instrument (model Link ISIS series 300) at the Scientific and Technological Research Equipment Center (STREC), Chulalongkorn University.

2.3.3 Density

The Archimedes method was used to measure the bulk density of sintered samples. The sample discs were firstly boiled in deionized water for 5 hours to release air in sample pores and then weighted in dry and wet condition using Precisa Gravimetrics AG (model R 2055M-DR) at Department of Chemistry, Faculty of Science, Chulalongkorn University. The relative density was calculated from the ratio of the measured bulk density to the theoretical density determined by XRD data.

2.3.4 Electrical conductivity measurement

The electrical conductivity of sintered samples was measured by a standard four-probe direct current (DC) technique under air condition. The sintered disc was cut into a rectangular bar with approximate dimensions of 5 mm x 12 mm x 1.5 mm. Four platinum wires were attached to the bar with platinum paste and fired at 950°C for 10 min with a heating rate of 5°C/min to obtain good electric contact as shown in Figure 2.2. The different voltage between two probes was recorded in a tube furnace at various temperatures in the range of 300 to 800°C with a heating rate of 5°C/min. The electrical conductivity was then calculated by following equation:

$$\sigma = (I/V)*(L/(W*T))$$



- Where σ is electrical conductivity (S/cm)
- I is fixed current (A)
- V is difference of measured voltage between two probes (V)
- L is distance between two voltage contact points (cm)
- T is thickness of rectangular bar (cm)
- W is width of rectangular bar (cm)

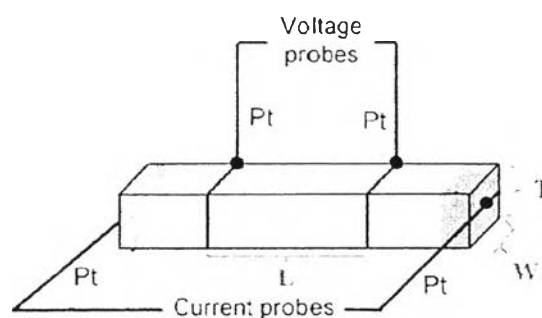


Figure 2.2 schematic diagram of specimen with four platinum (Pt) wire contacts

2.3.5 Oxygen permeation measurement

The discs were used as membranes for measurement of oxygen permeation flux. Each membrane was polished to the thickness of 0.7 mm with a diamond wheel, and then aligned with the two alumina tubes. Between the membrane and the tubes, ring-shaped Pyrex glass was placed as a sealing glass to prevent leakage. A seal was formed when the membrane and part of the alumina tubes were heated to 1000°C. The experimental set-up is shown in Figure 2.3.

Dry air (AR grade) and helium gas (99.999%) at a flow rate of 50 mL/min was fed to the membrane and the oxygen partial pressure gradient was achieved. The oxygen permeation measurement was carried out from high to low temperature in the range of 600 to 1000°C. The mixed gases of helium, used as the sweep gas, and permeated oxygen were then injected into the gas chromatography equipment (VARIAN, CP-3800) equipped with a molecular sieve 13X packed column and a thermal conductivity detector for determining the oxygen content.

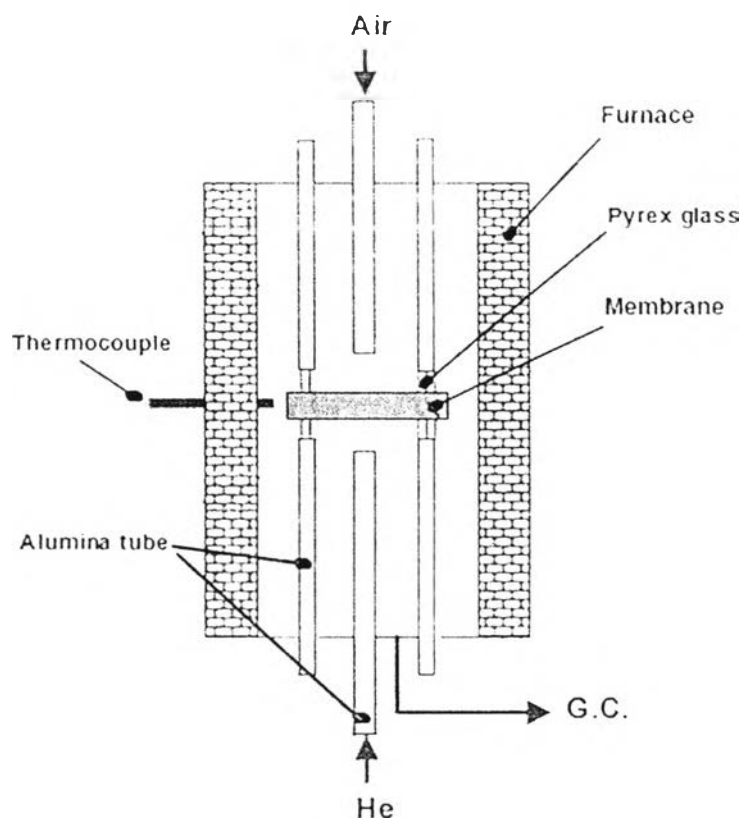


Figure 2.3 Cross-sectional view of the membrane reactor

2.3.6 Electrochemical measurement

Electrochemical performances and AC impedance analyses were evaluated on single cells at temperature between 600 and 800°C.

- Single Cell Performance Test

Single cell performances of various cathodes were evaluated with LSGM electrolyte and Ni-Fe oxide, as an anode precursor. All the electrode powders synthesized were mixed with STD-100 binder in a mass ratio of 1:1 and then painted onto both sides of the electrolyte surface by hand, followed by firing at 1000°C for 30 minutes to remove the organic solvent and complete the interface contact between electrolyte and electrodes. Pt meshes and wires were fabricated to each electrode as current collector. The schematic configuration of the test cell is shown in Figure 2.4.

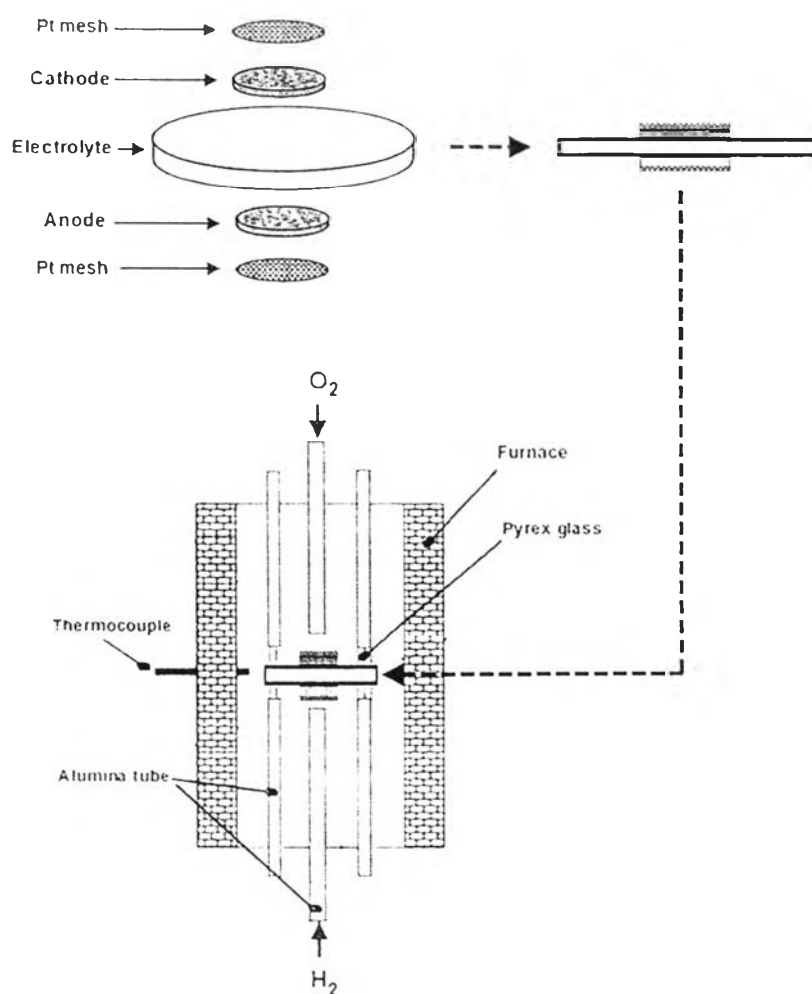


Figure 2.4 Schematic configuration of the single cell performance test set-up

The Ni-Fe anode was reduced to a metallic state at 800°C for 1 hour under H₂ flow before the cell performance measurement. During the operation, H₂ (99.999%) as fuel and O₂ (99.98%) as oxidant were supplied to the cathode and anode, respectively at a rate of 100 mL/min. Current-voltage (I-V) were measured with an AUTOLAB PGSTAT302N instrument using galvanostatic mode.

AC Impedance Measurement

AC impedance was analyzed in air by a potentiostat having a frequency response analyzer, and the test cell geometry and configuration were same as that used for the single cell performance test. The applied frequency ranged from 0.1 Hz to 10⁶ Hz with voltage amplitude of 10 mV.