CHAPTER III

EXPERIMENTAL

3.1 Chemicals

The chemicals listed in Table 3.1 and Table 3.2, were used without further purification.

Table 3.1 Reagents for synthesis of perovskites

Reagents	Formula Weight	Purity%	Company
$Ba(NO_3)_3$	99.999	261.35	Aldrich
$Co(NO_3)_2.xH_2O$	99.999	182.95	Aldrich
Citric Acid	192.12	99.5+	Aldrich
$Fe(NO_3)_3{\cdot}9H_2O$	404.00	99.99+	Aldrich
$Ga(NO_3)_3$	255.74	99.999	Alfa
HNO_3	63.01	70	Lab-Scan
$La(NO_3)_3{\cdot}6H_2O$	433.02	99.999	Aldrich
$NH_3.H_2O$	35.05	30	Panreac
Poly(vinyl alcohol)	50,000	99	Aldrich
$Sr(NO_3)_2$	211.63	99.995	Aldrich

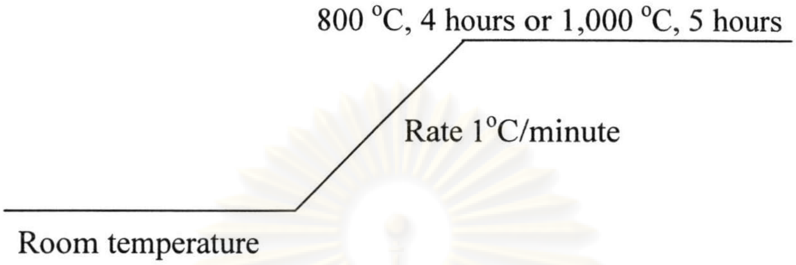
Table 3.2 Reagents for preparation of slurry coating compounds.

Reagents	Formula Weight	Purity%	Company
Dibutyl phthalate	278.35	99	Aldrich
Ethyl cellulose	-	48.0-49.5	Fluka
Fish oil	-	25% Omaga-3	Aldrich
Polyethylene glycol	8500-11500	-	Fluka
α - Terpineol	154.25	90	Aldrich

3.2 Preparations of perovskite powders by modified citrate method.

The perovskite powders, $La_{0.8}Sr_{0.2}Co_{0.6}Fe_{0.4}O_{3-\delta}$ (designated as LSCF 8264), $La_{0.6}Sr_{0.4}Ga_{0.3}Fe_{0.7}O_{3-\delta}$ (LSGF 6437) and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF 5582) were synthesized by using the modified citrate pyrolysis method. The catalytic perovskites, $La_{1-x}Sr_xCoO_{3-\delta}$, $La_{1-x}Sr_xFeO_{3-\delta}$, $Ba_{1-x}Sr_xCoO_{3-\delta}$ and $Ba_{1-x}Sr_xFeO_{3-\delta}$ (x = 0.2 - 0.6) were also prepared by the same method. Stoichiometric amounts of corresponding high purity metal nitrates (based on 0.02 mole of perovskite powder) in each composition as shown in Table 3.3 were partially dissolved into 10 ml ultra pure nitric acid (70 %). Then citric acid was added at a ratio of citric acid to metal ions (2:1). The mixture solution was then titrated with $NH_3.H_2O$ at the controlled rate of 2-3 ml/min. The pH value of the solution was adjusted to ~9. The solution changed from partially dissolved brown solution to clear brown solution. To prepare a basic homogeneous solution, a further $NH_3.H_2O$ titration (5 ml) was necessary after most of the metal nitrates were dissolved.

The homogeneous solution was carried out on a hot plate and the solution was dried at 200 °C by slowly heating temperature in a three-liter beaker covered with a fine sieve to prevent the loss of fine particle of powders. During combustion process, the homogeneous solution was agitated all the way. The water was evaporated until a sticky gel was obtained. Then it became a large swelling viscous mass and finally was self ignited by NH_4NO_3. The sponge-like solids expanded to occupy almost 2/3 of the beaker volume at the end. The resulting powder was ground by mortar and pestle, subsequently the synthesized perovskite oxide was calcined in a Carbolite RHF 1,600 muffle furnace. The condition used for the calcination of the perovskite powders was set as follows:



The particle was ground completely well by mortar before characterization. Calcined substrate powders were uniaxially compressed into disk. The substrate membranes were sintering in air. All the green discs were generally sintered in air at 1,100 °C, 10 hours for BSCF(5582), 1,300 °C, 10 hours for LSCF(8264) and LSGF(6437). The sintering conditions were as follows:

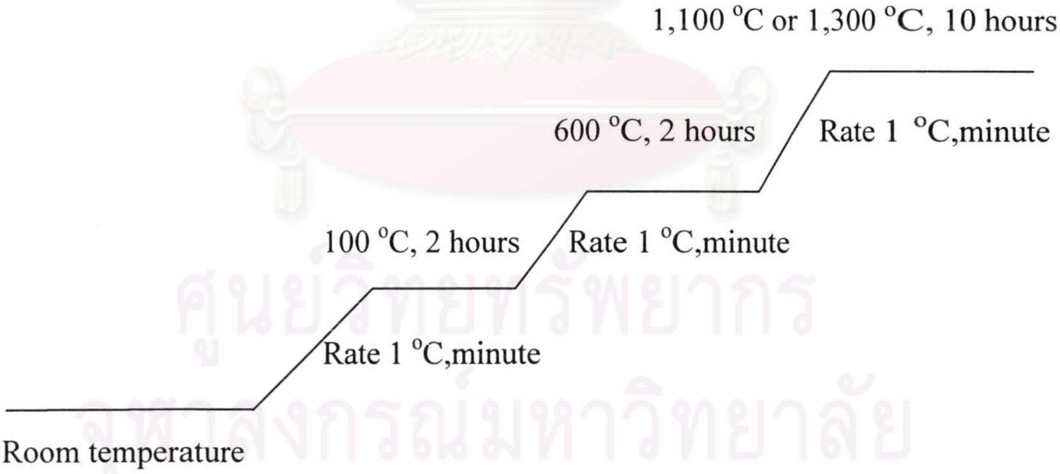


Table 3.3 Stoichiometric amounts of metal nitrates based on 0.02 mole of perovskite

Composition	Amounts of metal nitrates (g)					
	$La(NO_3)_3.6H_2O$	$Ba(NO_3)_3$	$Sr(NO_3)_2$	$Co(NO_3)_3.9H_2O$	$Ga(NO_3)_3$	$Fe(NO_3)_3.9H_2O$
$La_{0.8}Sr_{0.2}Co_{0.6}Fe_{0.4}O_{3-\delta}$	6.9283	-	0.8465	3.4924	-	3.2320
$La_{0.6}Sr_{0.4}Ga_{0.3}Fe_{0.7}O_{3-\delta}$	5.1962	-	1.6930	-	1.5344	5.6560
$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$	-	2.6135	2.1163	4.6565	-	1.6160
$La_{0.8}Sr_{0.2}CoO_{3-\delta}$	6.9283	-	0.8465	5.8206	-	-
$La_{0.7}Sr_{0.3}CoO_{3-\delta}$	6.0623	-	1.2698	5.8206	-	-
$La_{0.6}Sr_{0.4}CoO_{3-\delta}$	5.1962	-	1.6930	5.8206	-	-
$La_{0.5}Sr_{0.5}CoO_{3-\delta}$	4.3302	-	2.1163	5.8206	-	-
$La_{0.4}Sr_{0.6}CoO_{3-\delta}$	3.4642	-	2.5396	5.8206	-	-
$La_{0.8}Sr_{0.2}FeO_{3-\delta}$	6.9283	-	0.8465	-	-	8.08
$La_{0.7}Sr_{0.3}FeO_{3-\delta}$	6.0623	-	1.2698	-	-	8.08
$La_{0.6}Sr_{0.4}FeO_{3-\delta}$	5.1962	-	1.6930	-	-	8.08
$La_{0.5}Sr_{0.5}FeO_{3-\delta}$	4.3302	-	2.1163	-	-	8.08
$La_{0.4}Sr_{0.6}FeO_{3-\delta}$	3.4642	-	2.5396	-	-	8.08
$Ba_{0.8}Sr_{0.2}CoO_{3-\delta}$	-	4.1816	0.8465	5.8206	-	-

Table 3.3 Stoichiometric amounts of metal nitrates based on 0.02 mole of perovskite (cont.)

$Ba_{0.7}Sr_{0.3}CoO_{3-\delta}$	-	3.6989	1.2698	5.8206	-	-
$Ba_{0.6}Sr_{0.4}CoO_{3-\delta}$	-	3.1362	1.6930	5.8206	-	-
$Ba_{0.5}Sr_{0.5}CoO_{3-\delta}$	-	2.6135	2.1163	5.8206	-	-
$Ba_{0.4}Sr_{0.6}CoO_{3-\delta}$	-	2.0908	2.5396	5.8206	-	-
$Ba_{0.8}Sr_{0.2}FeO_{3-\delta}$	-	4.1816	0.8465	-	-	8.08
$Ba_{0.7}Sr_{0.3}FeO_{3-\delta}$	-	3.6989	1.2698	-	-	8.08
$Ba_{0.6}Sr_{0.4}FeO_{3-\delta}$	-	3.1362	1.6930	-	-	8.08
$Ba_{0.5}Sr_{0.5}FeO_{3-\delta}$	-	2.6135	2.1163	-	-	8.08
$Ba_{0.4}Sr_{0.6}FeO_{3-\delta}$	-	2.0908	2.5396	-	-	8.08

3.3 Perovskite membrane preparation.

A KBr die was used for the shape-forming process, which includes loading, pressing and ejecting. The die cavity was coated by wax and oil before the perovskite powders were loaded into the cavity. The powder was mixed into the binder by adding 1-2 % of polyvinyl alcolhol (PVA) and ground. The die having the perovskite powders inside was knocked against table 2-3 times to evaporate by air dry. After the die was completely assembled, the plunger was brought to the surface of the powders gently for final leveling and then rotates for smooth surface. The holder with mixed powder was pressed by the uniaxial pressing machine at 1 ton. The pressure was slowly released after 10 minutes, the green disc was produced around 1 mm thickness, 13 mm diameter from 500 mg of powder and the die was removed from the press.

3.4 Preparation of slurry coating compounds.

The calcined LSC, LSF, BSC, and BSF perovskite powders were mixed with an organic solvent, binders, plasticizer, and dispersant. The compositions were summarized in Table 3.4. The slurry compound was coated on both surfaces of the sintered membrane by a screen-printing method using 200-meshes screen. Post-heat treatment was conducted to remove the organic additives in muffle furnace. The condition used for the sintering of the coated membrane was set as follows:

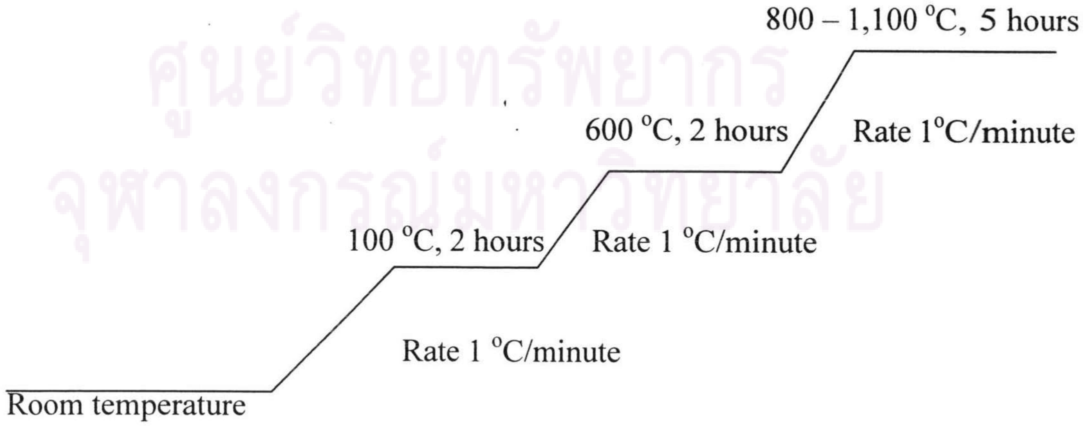


Table 3.4 The composition of slurry coating

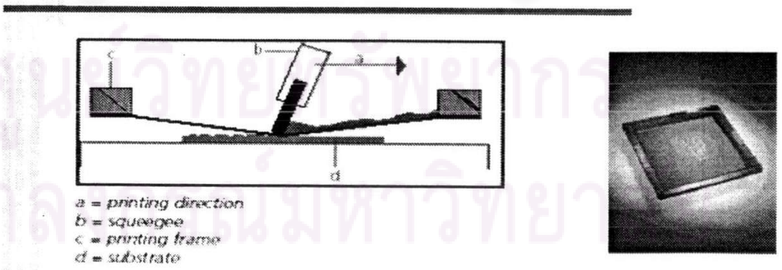
Solvent	A-Terpineol	85 %	60 %
Binder	Ethyl cellulose	7 %	
Dispersant	Fish oil %	2 %	
Plasticizer	PEG* +DBP**	6 %	
Ceramics	Perovskite powders		40 %

* Polyethylene glycol, ** Dibutyl phthalate

3.5 Screen printing method

The screen printing process was performed through stretching 200 porous meshes. A rubber-type blade (squeegee) was swept across the surface of the screen. A stencil mesh is cycle image with 13 mm diameter through the uncovered mesh to print the image. The coated substrate was manually placed onto watch glass for settle in an atmosphere and dried with heatgun. This method was repeated twice.

The printing plate for the screen printer is the screen a wooden frame with a fine nylon mesh stretched over it. The mesh is coated using 200-mashes screen.



Screen Printing Process

Printing Frame

Figure 3.1 Schematic diagrams of the screen printing process and printing frame.

3.6 Characterization of the perovskite oxide

3.6.1 X-ray diffractrometry (XRD)

The phase formations of perovskite powders and coated membranes were characterized after calcinations by XRD. Phase transformation of membrane coated and uncoated membranes were also characterized by XRD.

The XRD patterns, for either powder and membranes, were taken by using Rigaku, DMAX 2002 Ultima Plus X-ray powder diffractometer eqipped with a monochromator and a Cu-target X-ray tube (40 kV, 30 mA) and angles of 2θ ranged from 20-70 degree (step time 0.5 s., scan step 0.020°) at Department of Chemistry, Faculty of Science, Chulalongkorn University.

3.6.2 Scanning electron microscopy (SEM)

The morphology of the coated membrane was carried out using a JEOL JSM-5800LV scanning electron microscopy, the Oxford Instrument (Link ISIS series 300) at the Scientific and Technological Research Equipment Center (STREC), Chulalongkorn University. This instrument uses X-ray or electrons scattered back from the surface "illuminated" by a restored electron beam to generate an image with remarkable three-dimensional qualities. Specimens were sputter coated with gold to reduce charge effects.

3.6.3 Temperature-programmed desorption of O_2 (O_2-TPD)

Temperature-programmed desorption of O_2 was carried out in the in-house apparatus over 0.005 g of sample by using a Netzch STA.449C thermobalance. The perovskite powder was pretreated in He atmosphere (30 ml/min.) at 500 °C for 0.5 hours, then cooled to 100 °C, after which adsorption of gas was performed in a flow of O_2 (5.87 % balanced by He) for 40 minutes. The powder was maintained at 100 °C in He flow for another 0.5 hours to eliminate physically adsorbed O_2. Thereafter, the TPD was conducted by heating the sample to 800 °C at a rate 20 °C/min. Finally, the oxygen desorption was analyzed using gas chromatograph with a thermal conductivity detector (GC-TCD) for recording the O_2-TPD spectra.

3.6.4 Thermogravimetric analysis (TGA)

A themogravimetric experiment was performed on a TA instrument thermogravimetric analyzer (SDT 2960) at a heating rate of 20 °C/min. under N_2 atmosphere. A step temperature program was used to heat up from room temperature to 1,000 °C. In this experiment, the thermal analysis of the substrate and catalytic perovskite compounds were used powder.