

CHAPTER 3

EXPERIMENTAL STUDIES

The apparatus and experimental procedures include processing of perovskite membranes, disc-shape membrane reactor, and characterization of membrane materials, which are described as below:

3.1 Processing of Perovskite Discs.

3.1.1 General Procedure for Powder Preparation by a Modified Citrate Method

The powder preparation was modified from the citrate pyrolysis method [80, 81]. Stoichiometric amounts of corresponding high purity metal nitrates (based on 0.02 mole of perovskite powder) were dissolved in 10-ml ultrapure nitric acid (70%). All the chemicals were purchased from Aldrich Chemical Co., Inc. (Table 3.1) except as specified. Then citric acid with an amount of two times of the total metal ions was added. The nitrate solution was then titrated with NH_4OH at the controlled rate of 2-3 ml/min. The pH of the solution was adjusted to either 1-3.5 (acidic method) or ~ 9 (basic method), depending on the perovskite to be synthesized. To prepare a basic homogeneous solution, a further NH_4OH titration (5 ml) was necessary after most of the metal nitrates were dissolved.

All components, $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$, $\text{La}_{1-x}\text{Sr}_x\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ ($x = 0.4, 0.8$), $\text{La}_{0.2}\text{Ba}_{0.8}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$, $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Ga}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$, $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$, $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Ga}_{0.1}\text{Co}_{0.1}\text{Fe}_{0.8}\text{O}_{3-\delta}$, $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{0.4}\text{Fe}_{0.6}\text{O}_{3-\delta}$ ($x = 0.2, 0.4, 0.6$), $\text{La}_{0.4}\text{Sr}_{0.6}\text{Ga}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ ($y = 0.2, 0.4, 0.6$), and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Ga}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ ($y = 0.2, 0.4, 0.5, 0.6, 0.8$), were synthesized from basic solution. While $\text{La}_{0.6}\text{Sr}_{0.4}\text{Ga}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ was synthesized from pH in the range of 1-9.

Depending on each component, during the titration of the metal nitrate solutions with NH_4OH , the solutions were changed following the pH as shown in Table A in Appendix A.

For $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ compounds, the solution changed from partially dissolved brown solution to clear brown solution ($\text{pH}\approx 1$), to clear green solution ($\text{pH}\approx 1.5$), to green precipitated solution ($\text{pH}\approx 3-6$), to clear yellow solution ($\text{pH}\approx 7.5$), and finally to completely dissolved brown solution ($\text{pH}\approx 9$). Consequently, the pH of the solution was adjusted to ($\text{pH}\approx 1-3$), and ($\text{pH}\approx 6-9$) to obtain the homogeneous solution. The homogeneous solutions were agitated overnight.

Table 3.1 Reagent for synthesis of perovskite

Reagents	Purity%	Formula Weight	Company
$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	99.999	433.02	Aldrich
$\text{Sr}(\text{NO}_3)_2$	99.999	211.63	Aldrich
$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	99.99	404.00	Aldrich
$\text{Ga}(\text{NO}_3)_3$	99.999	255.74	Aldrich
$\text{Ba}(\text{NO}_3)_2$	99.999	261.35	Aldrich
$\text{Co}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$	99.999	182.95	Aldrich
Citric Acid	99.5	192.12	Aldrich
HNO_3	99.999	63.01	Aldrich
NH_4OH	A.C.S grade	35.05	J.T. Baker

The combustion of the homogeneous solution was carried out on a hot plate (Corning) at around 200°C in a three-liter beaker covered with a fine sieve to prevent the loss of the fine powders. The water was evaporated until a sticky gel was obtained. Then it became a large swelling viscous mass and finally self ignited by NH_4NO_3 . The combustion lasted for about 10-20 seconds. The sponge-like solids that expanded to occupy almost 2/3 of the beaker volume at the end were obtained mainly from the acid-

solution synthesis. While flake, or fine particles were formed from the basic-solution synthesis. This may be due to the amount of fuel (NH_4NO_3) in the basic solution, which was more than that in the acid solution. The resulting powder was ground by mortar and pestle, and then calcined in the air at 800-1,300 °C for 5 hours with heating and cooling rates of 2 °C/min to achieve phase purity or reduce the residual carbon. The particles were ground completely well by mortar before being subjected to characterization.

A list of the experimental conditions for synthesis of the perovskite compounds is given in Tables 3.2-3.10.



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Table 3.2 A list of the experimental conditions for synthesis of the perovskite compounds in the preliminary study

Materials	Reaction time(min) and solution color		Color and appearance changing during titration	pH	Spontaneous combustion time (sec) and material feature	Tc (°C)	Weight (g)		Weight loss (%)
	Nitric acid	Citric acid					Before	After	
SCF1082	3.30	4.00	brown to black to precipitate	9.15	22.00	-	3.3579		
	black	black	yellow brown precipitation		black powder	900	0.9596	0.7897	17.71
						1100	2.1120	1.7180	18.65
LSCF2828	3.40	5.15	red brown to green precipitate to red brown	9.35	Not available	-	3.3292		
	brown	red brown			fluffy black powder	800	0.8009	0.6674	15.15
						900	0.7994	0.6609	17.33
						1000	0.7943	0.6532	17.76
						1100	0.8034	0.6583	18.06
LBCF2828	3.00	4.00	dark brown to green brown to red brown	9.04	Not available	-	4.0082		
	orange	dark brow			fluffy black powder	800	0.9900	0.9248	6.58
	brown					900	1.0103	0.9408	6.88
						1000	1.0164	0.8906	12.38
BSCGF55118	24.00	5.00	orange to brown to black to green to golden brown to black brown (some solid)	9.04	18.69	-	2.4360		
	yellow	brown			fluffy black-brown powder	1100	0.9979	0.8530	14.52

Table 3.3 A list of the experimental conditions for synthesis of the perovskite compounds

Materials	Reaction time(min) and solution color		Color and appearance changing during titration	pH	Spontaneous combustion time (sec) and material feature	Tc (°C)	Weight (g)		Weight loss (%)
	Nitric acid	Citric acid					Before	After	
LSCFC6428	5.20	18	dark brown to precipitate to yellow precipitation to brown black	9.42	10.99	-	4.1628	1.2095	2.29
	orange brown	brown			black-brown network	1000	1.2379		
LSFG6482	5.0	18	black to green to yellow to precipitate to golden brown	9.11	11.09	-	3.9190	0.7088	0.44
	yellow	brown			fluffy bronze powder	700	0.7156	0.7267	1.38
BSFC5582	10.30	5.30	brown to green to black	9.39	28.72	-	3.7277	0.1969	
	brown	dark brown			fluffy brown powder	1000	1.2171	1.2132	19.83
BSFG5582	10.30	4.30	green to brown	9.33	21.66	-	3.1836	0.20	18.62
	yellow	brown (Ba solid)			fluffy black powder	1000	1.0571	1.0147	19.19

Table 3.4 A list of the experimental conditions for synthesis of $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{0.4}\text{Fe}_{0.6}\text{O}_{3.5}$ ($x = 0.2, 0.4, \text{ and } 0.6$) perovskites

Materials	Reaction time(hr) and solution color		Color and appearance changing during titration	pH	Spontaneous combustion time (sec) and material feature	Tc (°C)	Weight (g)		Weight loss (%)
	Nitric acid	Citric acid					Before	After	
LSGF8246	5	17	yellow to green to precipitate to yellow	9.23	13.78	-	4.0765		
	cream	brown			fluffy bronze-black powder	900	0.7235	0.6963	3.76
						1000	0.7144	0.6853	4.07
LSGF6446	5.15	16	yellow to green to precipitate to yellow brown	9.30	11.96	-	2.5618		
	yellow	brown			fluffy gray and bronze powder	900	0.7233	0.7044	2.61
						1000	0.6852	0.6682	2.48
LSGF4646	5	17	yellow to green to precipitate to brown	9.15	13.20	-	3.9126		
	yellow	brown			bronze-brown network	900	0.7298	0.7098	2.74
						1000	0.8193	0.7944	3.04

Table 3.5 A list of the experimental conditions for synthesis $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ ($x = 0.2, 0.4, 0.5, 0.6, \text{ and } 0.8$) perovskites

Materials	Reaction time(hr) and solution color		Color and appearance changing during titration	pH	Spontaneous combustion time (sec) and material feature	Tc (°C)	Weight (g)		Weight loss (%)
	Nitric acid	Citric acid					Before	After	
LSGF8228	5.00	18.0	black to yellow to green to precipitate to yellow brown	9.01	12.34	-	4.2925	0.6728	
	orange	brown			fluffy gray and bronze powder	900	1.8150	1.8108	0.23
						1050	1.8047	1.7923	0.69
LSGF6428	4	4.15	brown black to yellow to green to precipitate to yellow brown (fine yellow solid precipitated after 10 min)	9.05	10	-	4.3350		
	yellow	orange			fluffy bronze powder	800	0.9102	0.9102	0.16
		brown				900	0.9702	0.9686	0.16
						1000	0.9647	0.9608	0.43
LSGF5528	5.15	18	black to green to precipitate to yellow to golden brown	8.61	11.09	-	4.0279		
	yellow	brown			fluffy bronze powder	900	0.9786	0.9721	0.66
LSGF4628	5.00	18	black to green to precipitate to yellow	9.64	11.34	-	3.9291		
	yellow	brown			fluffy red-bronze powder	900	0.9084	0.8990	1.03
LSGF2828	5.20	17	dark brown to green to precipitation to green to yellow to brown	9.50	11.89	-	4.0031		
	lighter yellow	brown			fluffy bronze-brown powder	800	1.0890	1.0827	0.58

Table 3.6 A list of the experimental conditions for synthesis $\text{La}_{0.6}\text{Sr}_{0.4}\text{Ga}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ ($y = 0.2, 0.4, 0.5, 0.6, \text{ and } 0.8$) perovskites

Materials	Reaction time(hr) and solution color		Color and appearance changing during titration	pH	Spontaneous combustion time (sec) and material feature	Tc (°C)	Weight (g)		Weight loss (%)
	Nitric acid	Citric acid					Before	After	
LSGF6482	5.15	16	yellow to green to precipitation to yellow green	9.27	14.43	-	3.7230		
	yellow	orange					0.7515	0.7313	2.69
							0.6854	0.6637	3.17
LSGF6464	5	18	yellow to green to precipitation to-yellow	9.34	13.23	-	3.1268		
	yellow	brown					0.71590	0.7043	1.62
							7499	0.7274	3.00
LSGF6455	5	18	yellow to green to precipitation to yellow	9.21	14.13	-	2.7798		
	yellow	brown					0.7069	0.6892	2.50
							0.6896	0.6678	3.16
LSGF6446	5.15	16	yellow to green to precipitation to yellow to brown	9.30	11.96	-	2.5618		
	yellow	brown					0.7233	0.7044	2.61
							0.6852	0.6682	2.48
LSGF6428	4	4.15	orange brown to red brown (fine yellow solid precipitated after 10 min)	9.05	10	-	4.3350		
	yellow	orange					0.9102	0.9102	0.16
		brown					0.9702	0.9686	0.16
							0.9647	0.9608	0.43

Table 3.7 A list of the experimental conditions for synthesis $\text{La}_{0.4}\text{Sr}_{0.6}\text{Ga}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ ($y = 0.4, 0.6, \text{ and } 0.8$) perovskites

Materials	Reaction time(hr) and solution color		Color and appearance changing during titration	pH	Spontaneous combustion time (sec) and material feature	Tc (°C)	Weight (g)		Weight loss (%)
	Nitric acid	Citric acid					Before	After	
LSGF4664	7.50	12.0	black to brown to yellow to precipitation to green to yellow brown	9.10	14.18	-	4.0605	0.6042	
	orange	dark			fluffy bronze and black powder	900	1.9198	1.8916	1.47
		brown				1050	1.5365	1.4929	2.89
LSGF4646	5.00	18	black to green to precipitate to yellow to brown	8.55	10.76	-	3.8855		
	yellow	grown			fluffy bronze powder	900	0.9909	0.9740	1.71
LSGF4628	5.30	18	black brown to green	9.16	7.64		3.5215		
	yellow	brown	precipitation to green to yellow to brown to orange brown		fluffy bronze powder	700	0.7070	0.7060	0.14
						800	1.0536	1.0523	0.12
						900	0.7071	0.7046	0.35

Table 3.8 A list of the experimental conditions for synthesis $\text{La}_{0.6}\text{Sr}_{0.4}\text{Ga}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ prepared from different pH of nitrate solution

Materials	Reaction time(hr) and solution color		pH	Spontaneous combustion time (sec) and material feature	Tc (°C)	Weight (g)		Weight loss (%)
	Nitric acid	Citric acid				Before	After	
LSGF6482	23	24	0.80	9.02 fluffy yellow and gray powder	1300	0.6508 0.1662	0.1480	10.95
	yellow	orange	2.85	9.5 fluffy yellow and gray powder	1300	0.3755 0.1524	0.1323	13.19
			5.36	6.0 fluffy yellow and gray powder	1300	0.5467 0.1442	0.1145	20.60
			8.91	5.75 fluffy yellow and gray powder	1300	0.5968 0.2724	0.2031	25.44

Table 3.9 A list of the experimental conditions for synthesis $\text{La}_{0.6}\text{Sr}_{0.4}\text{Ga}_{0.2}\text{Fe}_{0.8}\text{O}_{3-8}$ prepared from different pH of nitrate solution

Materials	Reaction time(hr) and solution color		Color and appearance changing during titration	pH	Spontaneous combustion time (sec) and material feature	Tc (°C)	Weight (g)		Weight loss (%)
	Nitric acid	Citric acid					Before	After	
LSGF6428	5.30	18	black to yellow to green	1.36	4.80 fluffy bronze powder	900	0.8026	0.7159	10.80
	yellow	brown	black to yellow to green to precipitation	3.39	8.04 fluffy gray and brown powder	900	0.6503	0.6290	3.28
			black to green to precipitation to yellow- green some precipitation	7.65	9.48 fluffy gray and brown powder	900	0.7035	0.6524	7.26
LSGF6428	5.15	18	black to yellow to green to precipitation to brown	9.27	7.79 fluffy gray and brown powder	900	0.6943	0.6214	10.50
	yellow	brown	black to yellow brown	1.10	22.43 fluffy brown powder	900	0.7072	0.5749	18.71
			black to green	1.50	6.81 bronze sponge	1200	0.4484	0.3603	19.65
						900	0.6494	0.6346	2.28

Table 3.10 A list of the experimental conditions for calcination $\text{La}_{0.6}\text{Sr}_{0.4}\text{Ga}_{0.4}\text{Fe}_{0.6}\text{O}_{3-\delta}$ at different temperature

Materials	Reaction time(hr) and solution color		Color and appearance changing during titration	pH	Spontaneous combustion time (sec) and material feature	T _c (°C)	Weight (g)		Weight loss (%)
	Nitric acid	Citric acid					Before	After	
LSGF6446	5.15	16	yellow to green to precipitation to yellow brown	9.30	11.96	-	2.5618		
	yellow	brown					0.7233	0.7044	2.61
							0.6852	0.6682	2.48

Table 3.11 A list of the experimental conditions for calcination $\text{La}_{0.6}\text{Sr}_{0.4}\text{Ga}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ at different temperature

Materials	Reaction time(hr) and solution color		Color and appearance changing during titration	pH	Spontaneous combustion time (sec) and material feature	T _c (°C)	Weight (g)		Weight loss (%)
	Nitric acid	Citric acid					Before	After	
LSGF6428	4	4.15	orange brown to red brown (fine yellow solid precipitated after 10 min)	9.05	10	-	4.3350		
	yellow	orange					0.9102	0.9102	0.16
		brown					0.9702	0.9686	0.16
							0.9647	0.9608	0.43
							0.9565	0.9500	0.68
							0.3048	0.2997	1.67

T_c means calcination temperature

3.1.2 Powder Preparation by a Solid state Method

For synthesis of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Ga}_{0.1}\text{Co}_{0.1}\text{Fe}_{0.8}\text{O}_{3.8}$ by a solid state method, $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Ga}_{0.2}\text{Fe}_{0.8}\text{O}_{3.8}$ and $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3.8}$ were mixed with the ratio 1:1 by weight, ground in a mortar, and then calcined at $1,100^\circ\text{C}$ for 5 hours. The prepared particles were ground again before being subjected to characterization.

3.1.3 Membrane Preparation

A KBr die was used for the shape-forming process, which includes loading, pressing and ejecting. The powders were disaggregated by 5 ml of iso-propanol in ultrasonic bath for 30 minutes before being ground without binder by adding a couple drops of acetone or with binder by adding 1-2% of PVA, 2% of PEG 400, and 2-5% of water. The die cavity was coated by wax then by oil before the mixtures were loaded into the cavity. The die having mixtures inside was shrunk by lightly banging on the table for 2-3 times to allow the air inside the powders to escape. After the die was completely assembled, the plunger was brought to the surface of the powders gently for final leveling and then rotate to smooth the surface. About 5-7 ton pressure was then applied on the plunger of the die by the uniaxial pressing machine, which gave about $39,000\text{-}56,000\text{ kg/cm}^2$ pressure on the powders. At the beginning of the pressing, the pressure was slowly applied. After five minutes, the pressure was released and then the die was removed from the press. All the components were then stripped away except for the die assembly and plunger. Then the assembly was held while the press was slowly pumped until the pellet ejected. The produced green disc was about 1 mm thick and 13 mm diameter from 400-500 mg of powder, depending on the composition. Then the green discs were generally sintered in air at $1,250\text{-}1,350^\circ\text{C}$ for 5-20 hours, depending on the composition. The sintering conditions used were that the sample was heated to (1) 110°C for 3 hours with the heating rate 0.5°C/min. , (2) to 600°C with the same heating rate and kept at 600°C for 1-2 hrs, and (3) to $1,250\text{-}1,400^\circ\text{C}$ with the heating rate $1\text{-}2^\circ\text{C/min.}$ Finally the sample was cooled to room temperature with the cooling rate 2°C/min.

3.2 Disc –Shape Membrane Reactor

Due to the ease of fabrication and temperature control, disc-shaped membrane reactors are ideal for experiments to assess the membrane stability and its oxygen permeability. This section includes assembling disc-shaped membrane reactors, analyzing products, and operating reactors.

3.2.1 Joining of Ceramic Tubes and Perovskite Discs

The process of mounting a perovskite disc to a quartz tube has been developed. To separate oxygen from the air, the joint material has to be able to form an airtight bond with quartz and with perovskite, and to accommodate the thermal expansion mismatch between quartz and perovskite. It also has to be inert in an air and methane environment, and has a high melting or softening point, that can be specially applied to the high temperature partial oxidation of methane to syngas reaction. Gold, the most ductile element with a melting point of 1064°C and an inertness for most chemical reactions, fulfills the criteria mentioned above.

De Bruin et al. (1972) studied the mechanisms of noble metals and transition metals bonding on the ceramics. They showed a vacuum-tight bond between gold and Pyrex glass [82]. Bailey and Black (1978) described the methods for fabrication of some strong vacuum-tight bonds between gold and alumina [83]. Those methods were modified as follows: pure Au foils (99.99%, Aldrich) with thickness of 0.050 mm was cut into rings with 6 mm I.D./ 12 mm O.D. They were then cold-rolled to ensure flatness on the surface. A one-foot-long quartz tube with an extremely flat end was fire polished to remove the loose grains. The sintered perovskite discs with around 13 mm diameter were hand-polished by using carbide papers from grit 320 to 600 (Carbimet, trademark). The extra low-lint wiper (34155, Kimberly-Clark) was used to clean the surfaces of the discs. If needed, a resintering process would be applied to the perovskite discs. Immediately before use, one end of the quartz tubes for contacting with Au rings, Au rings, and perovskite discs were then cleaned with acetone by ultrasonic agitation for 20 min. Two more additional treatments were applied to the quartz tube and Au rings. They were

cleaned in 10% HNO₃ diluted with ethanol and then in 80°C hot water, each for 20 min, by ultrasonic agitation. The pieces were then air-dried or wiped by an extra low-lint wiper. Heat treatment was applied at 1030°C for three hours to remove the carbon deposited on the contact surface if strong bonding is required. A near 0.1 MNm⁻² pressure was applied by releasing an air-cooled spring (spring rate = 7.1 lbf/in) from the bottom of the ring to provide intimate contact for quartz/Au/perovskite joints while temperature was controlled at 1040°C for 10 hours (Eurotherm 818 programmer) with a 0.5°C/min heating rate to form the bonding. The nitrogen in the permeate side was checked by a gas chromatograph (HP5890 series II) during the annealing step. Until no nitrogen was detected in the helium flow, the furnace then was cooled to the temperature of interest at a 0.5°C/min cools rate. Experimental results showed that the air tight sealing could be sustained from 200°C to 1020°C and up to 0.4 atm pressure drop between permeate and feed sides, depending on the strength of the perovskite discs.

An inexpensive material, which was commonly used in the literature for sealing, was Pyrex glass. However, Tasi [56] found that the viscous glass covered part of the open area for O₂ permeation due to the surface tension and flow. It diffused into the grain boundaries, causing the disintegration of the membranes. Thus, pyrex-ring sealing was not suitable for long-term permeation or reaction studies in our reactor design.

3.2.2 Gas Chromatography Analysis

The inlet, the permeated oxygen and nitrogen were analyzed by the on-line gas chromatography (HP5890 series II) equipped with two automatic valves (Figure 3.1), a sampling valve and a by pass valve and HP Chemstation computer software for data collection and analysis.

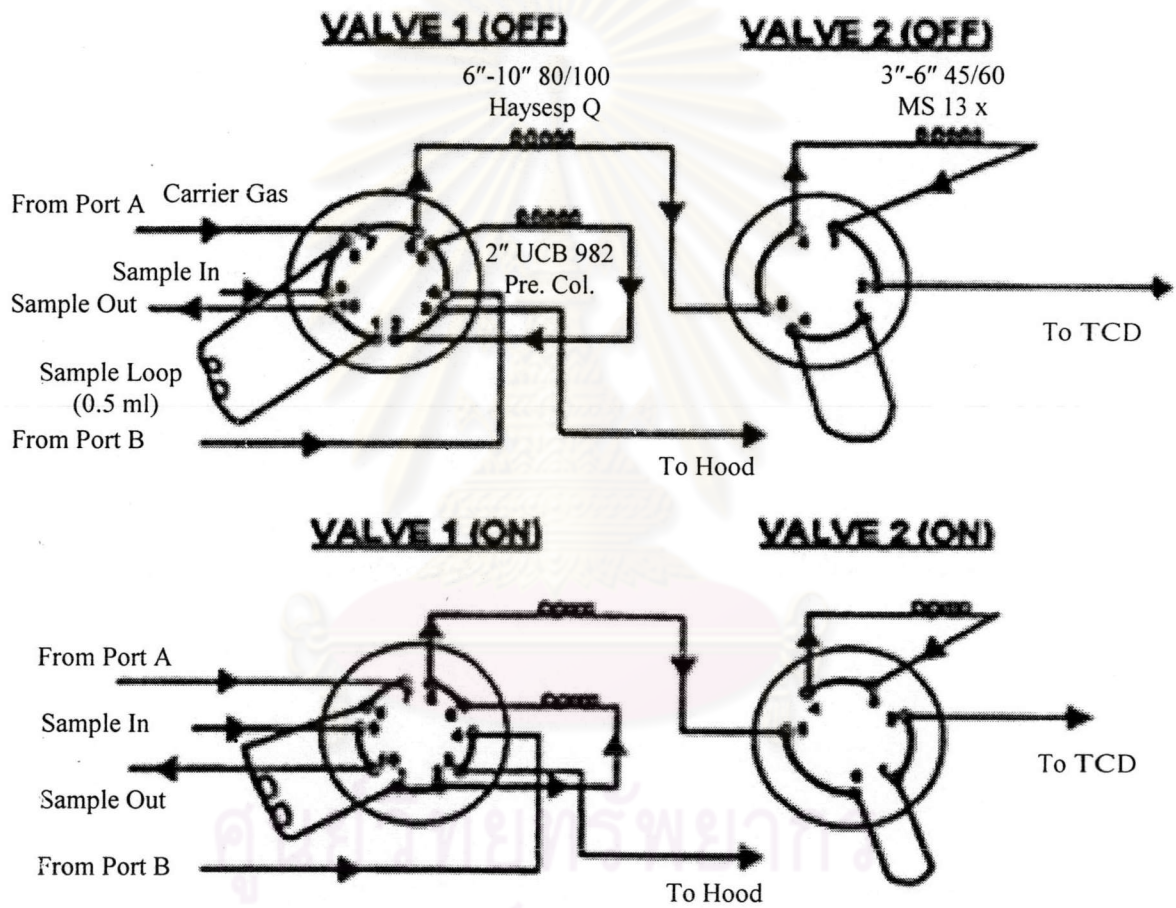


Figure 3.1 The configurations of on-line gas chromatography sampling system

A serial/bypass configuration was arranged for two isothermal columns (80°C) Hayesep Q and molecular sieve 13X. The valve two was set to off during the entire experiments because none of hydrocarbon gas was separated by Hayesep Q column. While the valve one was set to on and off for 30 seconds and 4 minutes, respectively, to allow injection of sample gases. The carrier gases directed the mixture of O₂ and N₂ through the Hayesep Q column, and then quickly entered the serial-arranged molecular sieve 13X, where those gases were separated and passed to the thermal conductivity detector. The inlet temperature, the oven temperature, and the detector temperature were set to 35, 35, and 120°C, respectively, for the good separation between those gases.

In the reaction experiments, the nitrogen concentration appeared to be the same magnitude as the oxygen concentration, indicating the porosity inside the membrane. An external standard was used for product analysis. The percentage by volume of the oxygen permeation was calculated from

$$\left[\frac{(\text{PAO}/40)}{(\text{PAO}/40) + (\text{PAN}/42)} \right] \times 100 \quad \begin{array}{l} \text{PAO} = \text{peak area of oxygen} \\ \text{PAN} = \text{peak area of nitrogen} \end{array} \quad (16)$$

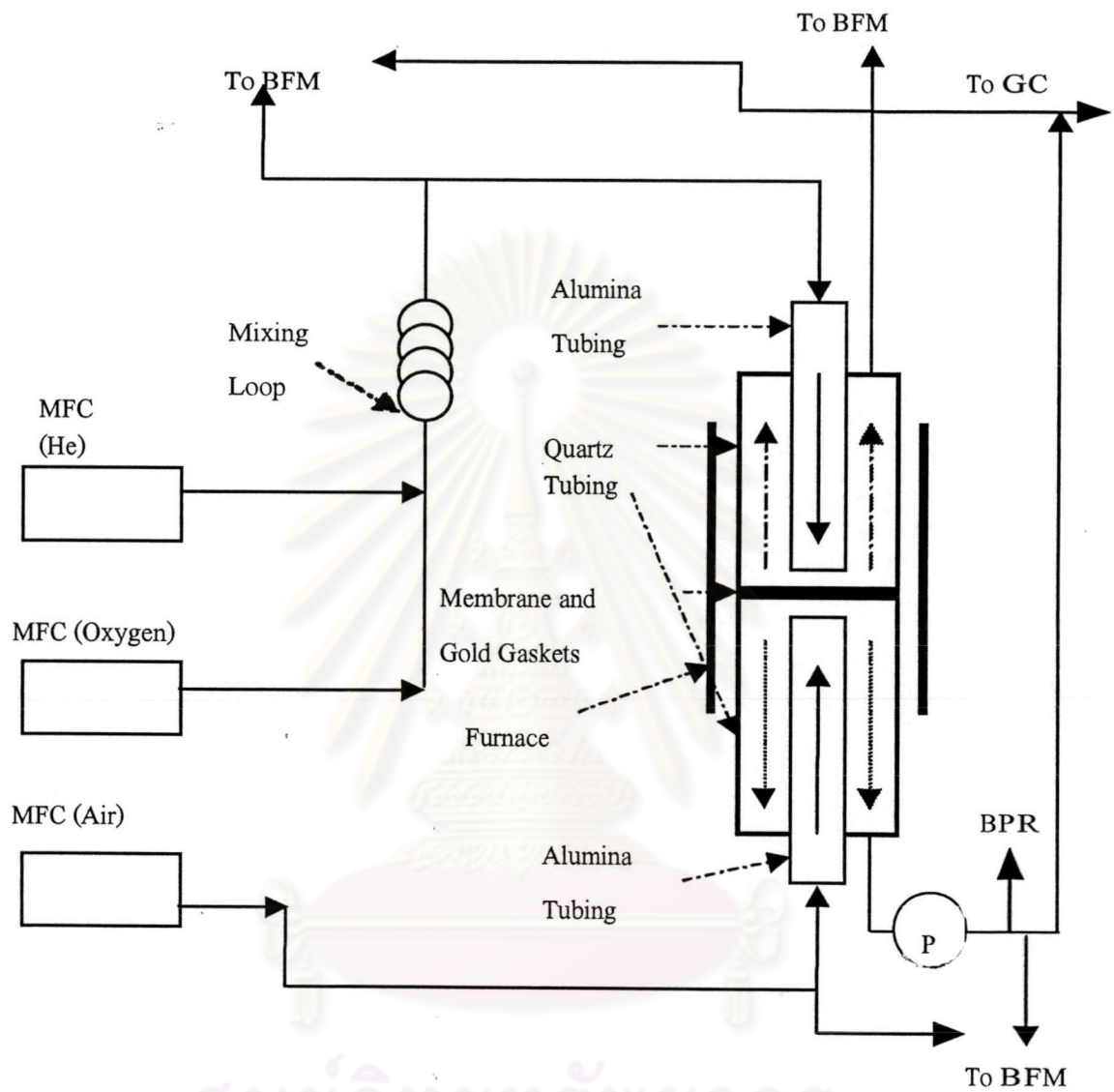
Where 40 and 42 (Equation 16) are the thermal response values generated by Rosie and Grob [84]. They determined relative response values for many of hydrocarbons and some oxygenated compounds to thermal conductivity detectors. They found that the response values were independent of temperature, carrier gas, flow rate, and concentration. These response values have an accuracy of about $\pm 3\%$.

3.2.3 Permeation Operation

Air (Airco) was used without further purification. Helium (Airco, < 99.9950%) flowed through an adsorptive oxygen trap (Oxy-Purge N[®], Alltech) to remove oxygen and moisture before being introduced to the system. The experimental layout is shown in Figure. 3.2. Mass flow controller (Brooks 5850C) calibrated by a digital bubble flow meter (Alltech) regulated the flow of gases into the reactor. An electronic pressure transducer (MKS Instrument Inc.) was used to accurately detect the reactor pressure, and a back-pressure regulator (Tescom Co.) was used to maintain the feed-side pressure to 780 mm Hg. A programmable temperature controller (Eurotherm 818 programmer) controlled a pre-calibrated vertical three-section furnace with thermocouple K (Omega), allowing the reaction zone to be operated isothermally or in a temperature programmed mode.

Details of membrane reactor design are shown in Figure 3.3. A sintered disc was polished to the thickness of interest and then mounted on a quartz tube using a gold ring seal. The final area of either side of membrane disc exposed to gasses was 0.283 cm². The diameters of the outer tube were 6 mm I.D./ 12 mm O.D. The clearance between the end of the central tube (2 mm I.D / 4 mm O.D.) in the reactor and the membrane surface was less than 3 mm for all of the cases. It was important to keep the clearance as small as possible to reduce the possible dead volume.

Before turning on the air, helium was flushed through the permeate side of the reactor until air was completely replaced. One side of the membrane disc was exposed to air (180 cm³/min), while the other side was exposed to pure helium (~ 30 cm³/min) in the permeation runs. The permeated gases were analyzed by on-line gas chromatography (HP 5890 Series II).



BFM: Bubble Flow Meter

MFC: Mass Flow Controller

BPR: Back Pressure Regulator

P : Pressure Transducer

Figure 3.2 Experimental layout

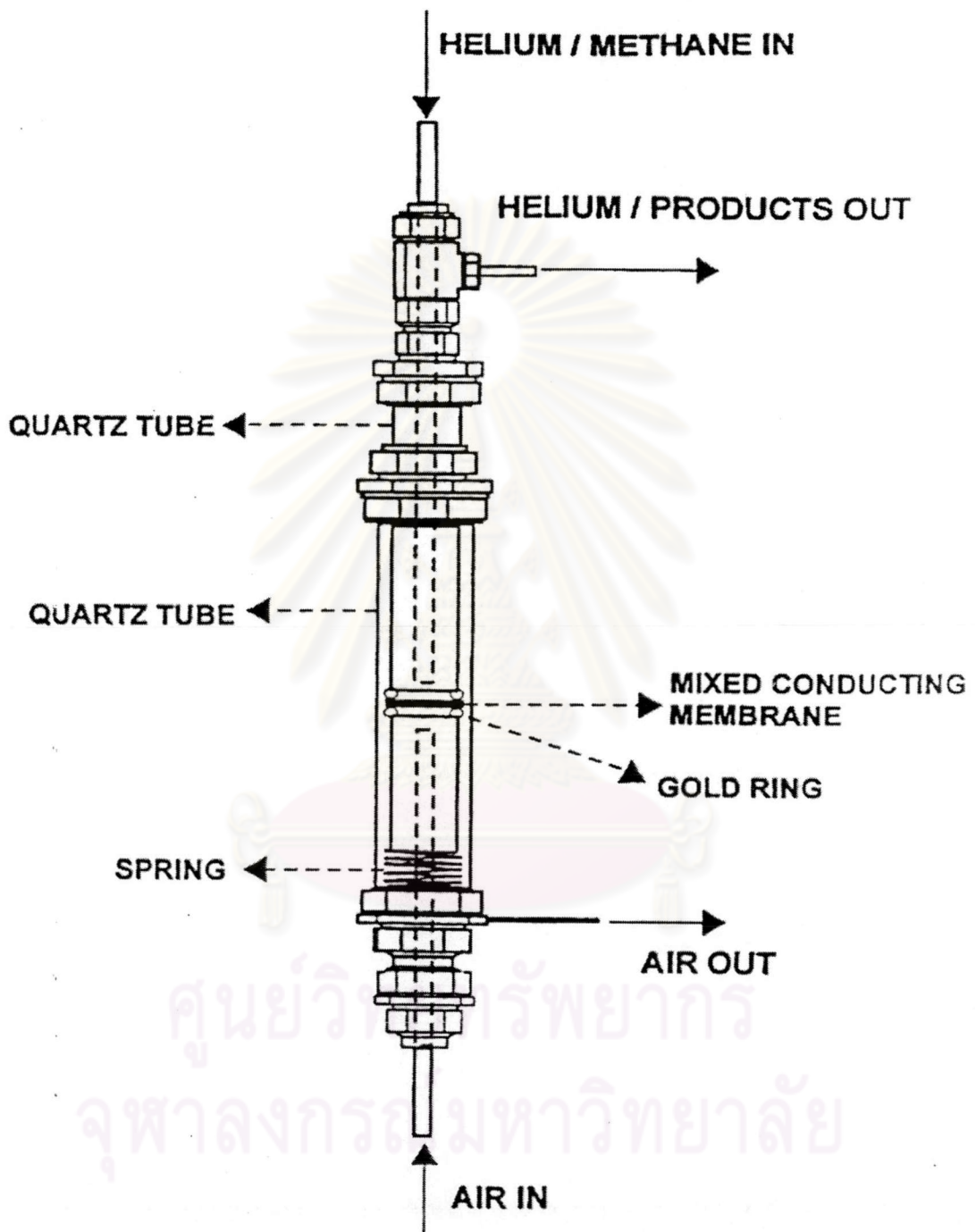


Figure 3.3 A Disc-shaped membrane reactor used in all experiments

3.3 Characterization of Membrane Materials

3.3.1 X-ray Diffraction (XRD) [85]

The X-ray patterns, for either powder or membranes, were taken by using General Electric diffractometer model XRD-5 with a graphite monochromator, using $\text{CuK}\alpha$ radiation (50kV/15 mA). Crystal quartz was used to calibrate the diffractometers before each experiment. The experiment diffraction patterns were collected at room temperature over a range of $20\text{-}80^\circ 2\theta$ (step-scanned at $0.1^\circ/1\text{ s}$ with a dwelling time 5 s). The quantitative analysis of crystalline phase concentrations was based on the comparison of observed peak heights after background subtraction. The value of the lattice parameter (a) for the (110), (200), (211), (220), (310), (222), (400), (411), and (420) reflections were plotted against $\sin^2\Theta$. An estimation of the lattice parameter was obtained by a linear extrapolation of such a plot, to the value at $\sin^2\Theta = 1$.

3.3.2 Scanning Electron Microscopy (SEM) [86]

The morphology of the powder and membrane discs was carried out using the SEM by AMRAY, AMR1610. This instrument uses X rays or electrons scattered back from the surface "illuminated" by a restored electron beam to generate an image with remarkable three-dimensional qualities.

Specimens, if necessary, were sputter coated with carbon to reduce charge effects. A scanning electron microscope with a thermionic tungsten cathode (4.1 A/cm^2 at 2820K) will has a final probe-diameter size of around 150 nm (lee 1993) under a probe current if $2 \times 10^{-8}\text{ S}$. The penetration of the electron beam depended on the density of the specimen and the acceleration voltage of the electron beam. Experiments performed under 15 KeV accelerating voltage corresponded to a depth in analysis of 0.3 μm for specimen.

3.3.3 Particle Size Analysis

Particle size measurements of powders were carried out by using a centrifugal particle size analyzer by Shimadzu, SA-CP2. The sample solutions were prepared by stirred 0.5 g of powder with 50 ml of NaHMP (hexametaphosphate). All parameters, including temperature, density of water and powder, and viscous of water, were set in the centrifuge mode of measuring condition. The density of powders was calculated from the molecular weight and the volume measured from the lattice parameter. The relative between sediment (stoke's law) and light intensity provided the particle size distribution in the range of 0.2 to 5 μm . The average particle size was the diameter at 50% by weight of powder and determined by plotting the cumulative percentage of the weight of powder with the diameter of particles in micron unit.

3.3.4 Density Measurement

Percentage theoretical densities were obtained to pre-screen the densities of the discs before further oxygen permeation rate measurements. The calculation of percent theoretical density is shown as follows:

$$\text{Bulk Density} = \frac{\text{Mass}}{\text{Bulk Volume}} \quad (17)$$

$$\% \text{ Relative Density} = \frac{\text{Bulk Density}}{\text{Theoretical Density}} \times 100 \quad (18)$$

Bulk volume (volume solids + volume porosity) can be measured by the disc geometrical shape. The dimensions and masses were measured by using a micrometer caliper and a sensitive analytical pan balance, respectively. For obtaining the theoretical density as shown in Appendix D, the dimensions can be calculated from the X-ray powder pattern. The oxygen nonstoichiometry δ was presumed to be from 0 to 0.5: therefore, a range of % theoretical density was obtained.