# CHAPTER 2

# EXPERIMENTAL PROCEDURE

This chapter provides the formation about chemical reagents, equipments and instruments which were used in this study. Moreover,experimental procedure and samples characterization were explained in detail.

## 2.1Chemical reagents, equipment and instruments

### 2.1.1 Chemical reagents

1) Hexachloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$) M.W.= 409.82 assay 37.5 0% Pt basis, Sigma
2) Cobalt (II) nitrate ($Co(NO_3)_2 \cdot 6H_2O$) M.W.= 291.04 assay 98.0%, Ajax
3) Chromium(III) nitrate ($Cr(NO_3)_3 \cdot 9H_2O$) M.W.= 400.15 assay 98.0%, Merck
4) Copper(II) nitrate ($Cu(NO_3)_2.3H_2O$) M.W.= 241.60 assay 99.5%,CaeloErba
5) Ferric(III) nitrate($Fe(NO_3)_3.9H_2O$) M.W. 404.02 assay 98.0%,CaeloErba
6) Nickel(II) nitrate($Ni(NO_3)_2 .6H_2O$) M.W.= 290.81 assay 99.0%, BDH
7) Potassium hydroxide (KOH) M.W.= 56.10 assay 85.5%,CaeloErba
8) Sodium borohydride($NaBH_4$) M.W.=37.83 assay 96%, Merck
9) Ethylene glycol ($HOCH_3CH_3OH$) F.W. = 62.07 assay 99.9%, J.T. Baker
10) Hydrogen peroxide ($H_2O_2$) F.W. 34.00 assay 30%wt in water, NCG
11) Carbon Vulcan XC-72,Fuel Cell Scientific
12) Carbon N115, Thai Carbon Black Public Co. LTD.
13) 5% Nafionin propanol solution, Electrochem. Inc.
14) Sulfuric Acid ($H_2SO_4$) F.W.= 98.08 assay 97.5%, J.T. Baker

15) Methanol($CH_3OH$) F.W.= 32.04 assay 99.0%, LAB SCAN

16) Ethanol ($CH_3CH_2OH$) F.W.= 46.07 assay 99.9%, MERCK

17) Isopropyl alcohol (($CH_3)_2CHOH$) F.W.= 60.10 assay 99.7%, LAB SCAN

18) 20%wt Platinum on Carbon Vulcan XC-72 (20% Pt/C), Fuel Cell Scientific

2.1.2 Equipments and instruments

1) Microwave oven 800W, R-26PS, Sharp
2) Microwaveoven 1100W, R-363P, Sharp
3) Fourier transform infrared spectroscopy (FTIR) 510, Nicolet
4) Powder X-ray diffraction (XRD) D500/D501,Siemen
5) Scanning electron microscopy (SEM) JSM-5910LV, JEOL
6) Scanning electron microscopy (SEM)JEM-6335FE, JEOL
7) Energy dispersive spectroscopy (EDS)INCA, The Microanalysis Suite Issue-16
8) Transmission electron microscopy (TEM) JEM-2010, JEOL
9) X-ray absorption spectrometry (XAS) beam line 8 at the Synchrotron Light Research Institute, Thailand
10) Cyclic voltammetry (CV)CV-50W, BAS
11) Single cell teststation, Department of Physic, Faculty of Science, Chiang Mai University

2.1.3Equipments for Single cell testing

1) Airbrush, Badger 155, Anthem

2)Nafion Membrane, NR-212, Ion Power.Inc.

3)Gas diffusion layer, GDL 34 AA, Ion Power.Inc.

4) Gaskets, SG-C10, Fuel Cell Earth

5) Bipolar plate, carbon graphite, ∅=3 cm, modified by Department of Physic, Faculty of Science, Chiang Mai University

**2.2 Experimentalprocedure**

In this research, 20% weights of platinum based ternary catalysts supported on carbon were prepared. The catalysts were PtCoCr, PtCoCu,PtCoFe, PtCoNi and PtCuNi. The ratio of platinum to other metals was varied as 2:1:1 and 6:1:1 by weight. The carbon supporters used in this research were carbon Vulcan XC-72 and carbon N115 which were modifiedthesurface by hydrogen peroxide before using as supporters for sample preparation. Three catalyst preparative methods which were microwave, reflux and $NaBH_4$ reduction methods were used.The prepared samples were represented by sample codes which identifiedthe metal type, carbon supporter, weight ratio of platinum: $metal_1$: $metal_2$, and also preparative method.

For example, Sample codes isPtCoCr(1)N(2)2(3)Mi(4)the letters and number in each part stand for their detail which are

Part (1) represents type of metalscontaining in the catalysts. In this case, the catalyst contains platinum, cobalt, and chromium.

Part (2) shown carbon type where Vu is untreated carbon Vulcan XC-72,V is treated carbon Vulcan XC-72 andN is treated carbon N115

Part (3) is weight ratio of metals which 2 denotes 2:1:1 where 6 is 6:1:1

Part (4) is preparative method which Mi, Re, and Na refer to microwave, reflux and $NaBH_4$ reduction methods respectively.

Thus, the code PtCoCrN2Mi represents the sample that contains platinum, cobalt, and chromium metal on treated carbon N115 with the metal ratio of 2:1:1. This sample is prepared by microwave method.

Theexperimental procedure of product preparation was separated into two main parts. The first part explainedabout the carbon treatment where the catalysts preparation was pointed in the second part.

### 2.2.1 Carbon supporter treatment

Two types of carbons, Vulcan XC-72 and carbon N115, were treated by the following method. In this part, hydrogen peroxide was used to modify carbon surface. First, carbon was cleaned with 2M sulfuric acidat 60 ˚C for 2 hours,then, washed with deionized water. After that, carbon was cleaned with 1M potassium hydroxide at 60 ˚C for 2 hours and washed the hydroxide ions out.The clean carbon was treated in 8N hydrogen peroxide for 48 hours at room temperature. Then, it was filtered, washed with deionized water, and dried in an oven. Finally, the treated carbon was investigated for functional groups by Fourier transform infrared spectroscopy.

### 2.2.2 Synthesis methods

Three synthesis methods; microwave, reflux and $NaBH_4$ reduction methods were applied to prepare platinum-based ternary catalysts supported on carbons.

**1) Microwave method**

Carbon was firstly added into ethylene glycol and pH 9 was obtained by adding potassium hydroxide.(The pH 9 was selected from concentration calculation of $OH^-$from equation 1.9. Morover,Joseyphus et.al [69] confirm that the concentration of $OH^-$at pH 9 can reduce thestandard reduction potential of ethylene glycol.In

preliminary, metals (such as Cu, Co, and Ni) were prepared by this method at pH 5, 7, 9, and 11. Particle precipitation by pH 9 occurred faster than other pH.It can be concluded that solution at pH 9 had better condition to prepare catalyst.) Then, stoichiometric amounts of metalprecursorswere added. After that, the mixture was placed in a microwave oven. The reaction used microwave power at 800 and 1100 W.The reaction was conducted using microwave cycle, time to on microwave and off microwave was called 1 microwave cycle. The reaction used 2 cycle types. First cycle, reduction time was on microwavefor50 second and off microwave 3 minutes, repeated 3 times. Second cycle,reduction time was on microwave for 60 second and off microwave 5 minutes, repeated for 10 times. The received powder was later filtered and dried in an oven.The catalysts prepared by this method consisted of PtCoCrV2Mi, PtCoCrVu2Mi, PtCuNiN2Mi, PtCuNiN6Mi,PtCuNiV2Mi, and PtCuNiV6Mi. Synthesis conditions for this method are shown in Table 2.1, which were metal precursors, % weight of metals, microwave power, reaction times, stop time and number of cycle.

2) **Reflux method**

The treated carbon was added into ethylene glycol at pH 9, which adjusted by adding potassium hydroxide. After that, stoichiometric amounts of metal precursors were added. The solution was reflux at 170 °C for 6 hours. The catalyst powders were filtered, washed with methanol and dried overnight in an oven. The catalysts prepared by this method were PtCoCrN2Re, PtCoCuN2Re, PtCoFeN2Re, PtCoNiN2Re, PtCuNiN2Re, PtCuNiN6Re,PtCuNiV2Re, and PtCuNiV6Re. Synthesis conditions which were metal precursors and % weight of metals, using in this method are shown in Table 2.2.

Table 2.1Synthesis conditions for microwave method

| Sample code | Metal precursors | %Weight of metal | Microwave power (W) | Reaction times (s.) | Stop times (min.) | No. of cycle |
|---|---|---|---|---|---|---|
| PtCoCrV2Mi | $H_2PtCl_6 \cdot xH_2O$ | 10 | 800 | 60 | 3 | 3 |
| | $Co(NO_3)_3 \cdot 6H_2O$ | 5 | | | | |
| | $Cr(NO_3)_3 \cdot 9H_2O$ | 5 | | | | |
| PtCoCrVu2Mi | $H_2PtCl_6 \cdot xH_2O$ | 10 | 800 | 60 | 3 | 3 |
| | $Co(NO_3)_3 \cdot 6H_2O$ | 5 | | | | |
| | $Cr(NO_3)_3 \cdot 9H_2O$ | 5 | | | | |
| PtCuNiN2Mi | $H_2PtCl_6 \cdot xH_2O$ | 10 | 1100 | 50 | 5 | 10 |
| | $Cu(NO_3)_2.3H_2O$ | 5 | | | | |
| | $Ni(NO_3)_2 .6H_2O$ | 5 | | | | |
| PtCuNiN6Mi | $H_2PtCl_6 \cdot xH_2O$ | 15 | 1100 | 50 | 5 | 10 |
| | $Cu(NO_3)_2.3H_2O$ | 2.5 | | | | |
| | $Ni(NO_3)_2 .6H_2O$ | 2.5 | | | | |
| PtCuNiV2Mi | $H_2PtCl_6 \cdot xH_2O$ | 10 | 1100 | 50 | 5 | 10 |
| | $Cu(NO_3)_2.3H_2O$ | 5 | | | | |
| | $Ni(NO_3)_2 .6H_2O$ | 5 | | | | |
| PtCuNiV6Mi | $H_2PtCl_6 \cdot xH_2O$ | 15 | 1100 | 50 | 5 | 10 |
| | $Cu(NO_3)_2.3H_2O$ | 2.5 | | | | |
| | $Ni(NO_3)_2 .6H_2O$ | 2.5 | | | | |

**3) $NaBH_4$ reductionmethod**

First, the treated carbon was added into ethylene glycol at pH 9, which adjusted by adding potassium hydroxide. Then, stoichiometric amounts of metal precursors were added. After that, stoichiometric amount of sodium borohydride powder was added for a reduction process and the reaction was stirredfor 24 hours. The final powders were filtered, washed with methanol and dried overnight in oven. The catalysts prepared by this method consisted of PtCoCrV2Na, PtCoCrVu2Na, PtCuNiN2Na, PtCuNiN6Na,PtCuNiV2Na, and PtCuNiV6Na. Synthesis conditions which were metal precursors and % weight of metals, using in this method are shown in Table 2.3.

First types of catalysts were prepared in this research using two types of carbon, two ratios for metals, and three methods. The summary table of all prepared catalysts shows in Table 2.4.

Table 2.2Synthesis conditions for reflux method

| Sample code | Metal precursors | %Weight of metal |
|---|---|---|
| PtCoCrN2Re | $H_2PtCl_6 \cdot xH_2O$ | 10 |
| | $Co(NO_3)_3 \cdot 6H_2O$ | 5 |
| | $Cr(NO_3)_3 \cdot 9H_2O$ | 5 |
| PtCoCuN2Re | $H_2PtCl_6 \cdot xH_2O$ | 10 |
| | $Co(NO_3)_3 \cdot 6H_2O$ | 5 |
| | $Cu(NO_3)_2.3H_2O$ | 5 |
| PtCoFeN2Re | $H_2PtCl_6 \cdot xH_2O$ | 10 |
| | $Co(NO_3)_3 \cdot 6H_2O$ | 5 |
| | $Fe(NO_3)_3.9H_2O$ | 5 |
| PtCoNiN2Re | $H_2PtCl_6 \cdot xH_2O$ | 10 |
| | $Co(NO_3)_3 \cdot 6H_2O$ | 5 |
| | $Ni(NO_3)_2 .6H_2O$ | 5 |
| PtCuNiN2Re | $H_2PtCl_6 \cdot xH_2O$ | 10 |
| | $Cu(NO_3)_2.3H_2O$ | 5 |
| | $Ni(NO_3)_2 .6H_2O$ | 5 |
| PtCuNiN6Re | $H_2PtCl_6 \cdot xH_2O$ | 15 |
| | $Cu(NO_3)_2.3H_2O$ | 2.5 |
| | $Ni(NO_3)_2 .6H_2O$ | 2.5 |
| PtCuNiV2Re | $H_2PtCl_6 \cdot xH_2O$ | 10 |
| | $Cu(NO_3)_2.3H_2O$ | 5 |
| | $Ni(NO_3)_2 .6H_2O$ | 5 |
| PtCuNiV6Re | $H_2PtCl_6 \cdot xH_2O$ | 15 |
| | $Cu(NO_3)_2.3H_2O$ | 2.5 |
| | $Ni(NO_3)_2 .6H_2O$ | 2.5 |

Table 2.3 Synthesis conditions for $NaBH_4$ reduction method

| Sample code | Metal precursors | %Weight of metal |
|---|---|---|
| PtCoCrV2Na | $H_2PtCl_6 \cdot xH_2O$ | 10 |
| | $Co(NO_3)_3 \cdot 6H_2O$ | 5 |
| | $Cr(NO_3)_3 \cdot 9H_2O$ | 5 |
| PtCoCrVu2Na | $H_2PtCl_6 \cdot xH_2O$ | 10 |
| | $Co(NO_3)_3 \cdot 6H_2O$ | 5 |
| | $Cr(NO_3)_3 \cdot 9H_2O$ | 5 |
| PtCuNiN2Na | $H_2PtCl_6 \cdot xH_2O$ | 10 |
| | $Cu(NO_3)_2.3H_2O$ | 5 |
| | $Ni(NO_3)_2 .6H_2O$ | 5 |
| PtCuNiN6Na | $H_2PtCl_6 \cdot xH_2O$ | 15 |
| | $Cu(NO_3)_2.3H_2O$ | 2.5 |
| | $Ni(NO_3)_2 .6H_2O$ | 2.5 |
| PtCuNiV2Na | $H_2PtCl_6 \cdot xH_2O$ | 10 |
| | $Cu(NO_3)_2.3H_2O$ | 5 |
| | $Ni(NO_3)_2 .6H_2O$ | 5 |
| PtCuNiV6Na | $H_2PtCl_6 \cdot xH_2O$ | 15 |
| | $Cu(NO_3)_2.3H_2O$ | 2.5 |
| | $Ni(NO_3)_2 .6H_2O$ | 2.5 |

**2.3 Materials characterizations**

Both treated and untreated carbons were characterized by FT-IR technique to confirm functional groups on the carbon surface. The catalysts were characterized their physical properties by using XRD, SEM, EDS, TEM and XAS techniques. The electrochemical properties of catalysts were examined by CV and single cell testing technique.

Table 2.4 Sample codes, catalysts type, carbon type, weight ratio of metal and synthesis methods for all catalysts.

| Sample codes | Catalyst | Carbon type | Metal ratio | Method |
|---|---|---|---|---|
| PtCoCrV2Mi | Pt-Co-Cr | treated carbon Vulcan XC-72 | 2:1:1 | microwave |
| PtCoCrVu2Mi | Pt-Co-Cr | untreated carbon Vulcan XC-72 | 2:1:1 | microwave |
| PtCoCrV2Na | Pt-Co-Cr | treated carbon Vulcan XC-72 | 2:1:1 | $NaBH_4$ reduction |
| PtCoCrVu2Na | Pt-Co-Cr | untreated carbon Vulcan XC-72 | 2:1:1 | $NaBH_4$ reduction |
| PtCoCrN2Re | Pt-Co-Cr | treated carbon N115 | 2:1:1 | reflux |
| PtCoCuN2Re | Pt-Co-Cu | treated carbon N115 | 2:1:1 | reflux |
| PtCoFeN2Re | Pt-Co-Fe | treated carbon N115 | 2:1:1 | reflux |
| PtCoNiN2Re | Pt-Co-Ni | treated carbon N115 | 2:1:1 | reflux |
| PtCuNiN2Mi | Pt-Cu-Ni | treated carbon N115 | 2:1:1 | microwave |
| PtCuNiN2Re | Pt-Cu-Ni | treated carbon N115 | 2:1:1 | reflux |
| PtCuNiN2Na | Pt-Cu-Ni | treated carbon N115 | 2:1:1 | $NaBH_4$ reduction |
| PtCuNiN6Mi | Pt-Cu-Ni | treated carbon N115 | 6:1:1 | microwave |
| PtCuNiN6Re | Pt-Cu-Ni | treated carbon N115 | 6:1:1 | reflux |
| PtCuNiN6Na | Pt-Cu-Ni | treated carbon N115 | 6:1:1 | $NaBH_4$ reduction |
| PtCuNiV2Mi | Pt-Cu-Ni | treated carbon Vulcan XC-72 | 2:1:1 | microwave |
| PtCuNiV2Re | Pt-Cu-Ni | treated carbon Vulcan XC-72 | 2:1:1 | reflux |
| PtCuNiV2Na | Pt-Cu-Ni | treated carbon Vulcan XC-72 | 2:1:1 | $NaBH_4$ reduction |
| PtCuNiV6Mi | Pt-Cu-Ni | treated carbon Vulcan XC-72 | 6:1:1 | microwave |
| PtCuNiV6Re | Pt-Cu-Ni | treated carbon Vulcan XC-72 | 6:1:1 | reflux |
| PtCuNiV6Na | Pt-Cu-Ni | treated carbon Vulcan XC-72 | 6:1:1 | $NaBH_4$ reduction |

### 2.3.1 Fourier transform infrared spectroscopy (FT-IR)

Both carbons were characterized their functional groups by Fourier transform infrared spectroscopy. The samples were diluted by potassium bromide and operated in the wavelength range of 400-4000 $cm^{-1}$ for FT-IR analysis.

### 2.3.2 X-ray diffraction (XRD)

All prepared catalysts werefirstly characterized by powder X-ray diffraction for phase identification.The instrument used Cu $K_\alpha$ radiation ($\lambda$ = 1.5418Å) operating at 20 kV-15mA, with a scanning rate of 0.04°/s in the 2θ range of 10°-80°.The sample identification was assisted by STOE Win XPOW Computer Software (search-match program).

### 2.3.3 Scanning electron microscopy (SEM) equipped with energy dispersive spectroscopy (EDS)

The morphology of the all products was analyzed by scanning electron microscopy, SEM, JEOL JSM-5910LV and JEM-6335FE, JEOL operating at 15 kV as accelerating voltage. Type and percent weight of element were analyzed byenergy dispersive spectroscopy, EDS, (INCA, The Microanalysis Suite Issue-16). For SEM-EDS sample preparation, samples were dropped on conductive carbon tape which attached to the SEM stubs.

### 2.3.4Transmission electron microscopy (TEM)

The morphology and structure of all products were also characterized by transmission electron microscope, JEOL model JEM-2010 operating at 20 kV. The

samples were prepared by dispersing a small amount of sample in absolute ethanol and put same droplets of the solutions onto copper grids coated with holey carbon films and letting the ethanol evaporate slowly under a lamp.

**2.3.5 X-ray absorption spectrometry (XAS)**

. The X-ray absorption spectrometerlocated atbeam line 8 in the synchrotron light research institute was performed in this study. The catalystsfrom condition PtCoCrVu2Mi, PtCoCrV2Mi, PtCoCrVu2Na and PtCoCrV2Na were characterizedby this technique. The XASwas applied to identify the oxidation state and local structure of metals.The XAS operated photon energy for cobalt between 7600 to 8400 eV and chromium between5900 to 8400 eV.To prepare sample for testing, the sample powder was added in testing cell and cover cell with kapton tape.

**2.3.6 Cyclic voltammetry (CV)**

Electrochemically testing by cyclic voltammetry technique was performed.The catalysts from condition PtCoCrVu2Mi, PtCoCrV2Mi, PtCoCrVu2Na and PtCoCrV2Na werestudied bythis technique. The glassy carbon disk, Ag/AgCl and Pt wire were used as working, reference and auxiliary electrodes, respectively. While 1.00 M $H_2SO_4$was used as electrolyte. To prepare working electrode, 10 milligrams of supported catalyst was sonicated in mixed 0.5 milliliters of deionized water and 0.06 milliliters of 5% Nafion solution (Electrochem, Inc.) for 30 minutes. Then, 10 microliters of the homogenous solution were dropped on glassy carbon disk electrode (∅= 5 mm,area = 0.196 $cm^2$) and allowed to dry in oven at 70 ˚C for 30 minutes. After that, 5 microliters of 5% Nafion solution were dropped on glassy carbon surface again

and dried at 70˚C for 10 minutes in oven. Cyclic voltammograms were operated between 0 to 1.2 V (vs. Ag/AgCl) at a scan rate of 20mVs$^{-1}$ for 30 cycles.

**2.3.7 Single cell testing**

The electrochemical performance investigation was performed by single cell testing located at THEP center building,Department of Physics, Faculty of Science, Chiang Mai University which shown in Figure 2.1.The catalysts from condition PtCoCuN2Re, PtCoNiN2Na, PtCoNiN6Na, PtCoNiV2Na, PtCoNiV6Na, PtCoNiN2Re, PtCoNiN6Re, PtCoNiV2Re and PtCoNiV6Re werestudied by this technique. The single cell was prepared by 4 steps which were 1) micro-porous layer2) membrane treatment3) catalyst inkand 4) catalyst coated membrane.

Figure 2.1 Single cell test station

1)Micro-porous layer was prepared by spraying suspension of mixed 0.05 g of carbon black, 8 ml of propyl alcohol and 0.6 ml of 5% Nafionsolution on GDL (Figure 2.2a). The GDL was then dried at 70 ˚C for 1 hour in oven.

2)For membrane treatment, the membrane (Nafion NR-212) was cleaned with hydrogen peroxide at 70 ˚C for 2 hours. Then, it was washed by deionized water at 70 ˚C for 2 hours. Next, the membrane was treated with 1 M sulfuric acidat 70 ˚C for 2 hours. Finally, it was washed by deionized water at 70 ˚C for 2 hours. and kept in deionized water before using.

3) For the catalyst ink preparation, the catalyst ink was prepared by mixing 0.05 g of catalyst, 8 ml of propyl alcohol and 0.6 ml of 5% Nafion solution. The mixture was sonicated for 30 minutes.

4)Catalyst coated membrane (CCM) (Figure 2.2b) was preparedby using the commercial 20% Pt/C for both anode and cathode, called commercial cell. Where using commercial catalysts for anode side and prepared catalyst for cathode side was called prepared cell.In preparative process, the catalyst ink was firstly sprayed on membrane which put over a hotplate at 70 ˚C. The ink was sprayed with nitrogen as the driving gas. One membrane side hassprayed catalyst area about 1 $cm^2$ and nearly 0.4 mg /$cm^2$ for catalyst loading. After one side was finished, the membrane was dried at 70 ˚C for 5 minutes. The other membrane side was sprayed with catalyst ink with the same methodand dried at 70 ˚C for 5 minutes. Finally, the membrane was ready to test with the single cell testing.

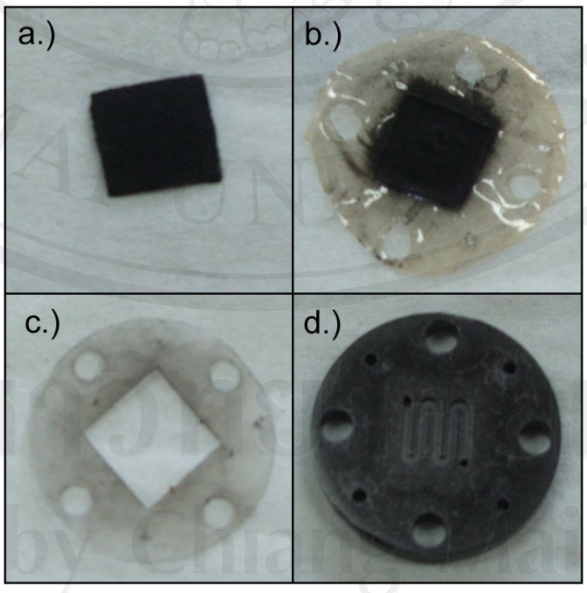


Figure 2.2 Components of Single cell: GDL(a), CCM(b), Gasket(c) and Bipolar plate(d)

Single cell testing technique was used to comparethe electro-catalyst activity between commercial cell and prepared cell. The single cell was prepared by sandwiching the CCM with GDL's, gaskets (Figure 2.2c) and bipolar plate(Figure 2.2d). The cell used hydrogen gas at anode side and oxygen gas at cathode side. The gas pressure was 50 sccm. for both sides. The single cell was operated at current density about 0.0 to 1.0 A for four times at room temperature and 1 atm.

Techniques used for each catalyst were summarized in table 2.5.

Table 2.5 Physical and electrochemical testing applied for all prepared catalysts.

| Sample codes | XRD | SEM | EDS | TEM | XAS | CV | Single cell test |
|---|---|---|---|---|---|---|---|
| PtCoCrV2Mi | ⁄ | ⁄ | ⁄ | ⁄ | ⁄ | ⁄ | |
| PtCoCrVu2Mi | ⁄ | ⁄ | ⁄ | ⁄ | ⁄ | ⁄ | |
| PtCoCrV2Na | ⁄ | ⁄ | ⁄ | ⁄ | ⁄ | ⁄ | |
| PtCoCrVu2Na | ⁄ | ⁄ | ⁄ | ⁄ | ⁄ | ⁄ | |
| PtCoCrN2Re | ⁄ | ⁄ | ⁄ | ⁄ | | | |
| PtCoCuN2Re | ⁄ | ⁄ | ⁄ | ⁄ | | | ⁄ |
| PtCoFeN2Re | ⁄ | ⁄ | ⁄ | ⁄ | | | |
| PtCoNiN2Re | ⁄ | ⁄ | ⁄ | ⁄ | | | |
| PtCuNiN2Mi | ⁄ | ⁄ | ⁄ | ⁄ | | | |
| PtCuNiN2Re | ⁄ | ⁄ | ⁄ | ⁄ | | | ⁄ |
| PtCuNiN2Na | ⁄ | ⁄ | ⁄ | ⁄ | | | ⁄ |
| PtCuNiN6Mi | ⁄ | ⁄ | ⁄ | ⁄ | | | |
| PtCuNiN6Re | ⁄ | ⁄ | ⁄ | ⁄ | | | ⁄ |
| PtCuNiN6Na | ⁄ | ⁄ | ⁄ | ⁄ | | | ⁄ |
| PtCuNiV2Mi | ⁄ | ⁄ | ⁄ | ⁄ | | | |
| PtCuNiV2Re | ⁄ | ⁄ | ⁄ | ⁄ | | | ⁄ |
| PtCuNiV2Na | ⁄ | ⁄ | ⁄ | ⁄ | | | ⁄ |
| PtCuNiV6Mi | ⁄ | ⁄ | ⁄ | ⁄ | | | |
| PtCuNiV6Re | ⁄ | ⁄ | ⁄ | ⁄ | | | ⁄ |
| PtCuNiV6Na | ⁄ | ⁄ | ⁄ | ⁄ | | | ⁄ |