REMOVAL OF CARBON MONOXIDE FROM HYDROGEN GAS USING PLATINUM AND PALLADIUM CATALYST IN ELECTROCHEMICAL WATER GAS SHIFT REACTION

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I would like to dedicate this thesis to my beloved husband, ayah, maa and the rest of my family members for their encouragement and the advices throughout the journey and of course to my son Muhammad Anas who is born during ummi is struggling to finish this thesis. Thank you for being born and you give me the priceless experiences

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ABSTRACT

Proton exchange membrane fuel cell (PEM-FC) uses hydrogen as the feed gas and converts it directly into electrical energy. However, the high performance of PEM fuel cell is degraded as the accumulated carbon monoxide (CO) conquers the active sites of the anode catalyst which solely belongs to hydrogen molecules. This research focused on the application of PEM fuel cell as an electrochemical (CO) converter. The reversible concept of fuel cell was utilized to convert the CO to carbon dioxide (CO_2) as to obtain a tolerance concentration of CO. The electrochemical CO converter underwent the electrochemical water gas shift reaction (EWGSR) in order to convert the CO to CO_2. Five membrane electrode assemblies (MEA) samples with different ratios of platinum (Pt) to palladium (Pd) on activated carbon (Ac) and coated on polybenzimidazole (PBI) membrane were prepared. The Pt-Pd/Ac MEA samples were in the range of 1:0 to 1:4 which represent Pt:Pd ratios. The samples were tested by using hydrogen-rich gas (CO/H_2) with 100 ppm of CO. The PBI membrane was used for electrochemical CO converter as it is cheaper and can tolerate the CO without controlling the humidity content. The process parameters were CO/H_2 flow rate, voltage of power supply and operating temperature of electrochemical CO converter. The performance of the sample was found to increase at three operating conditions which is the CO/H_2 gas flow rate is 50 ml/min with 0.7V voltage at room temperature. The result was 96.73% of CO conversion.

ABSTRAK

Membran penukaran proton sel bahan api (PEM-FC) menggunakan hidrogen gas sebagai gas suapan dan ia ditukarkan secara terus kepada tenaga elektrik. Walau bagaimanapun, membran penukaran proton sel bahan api yang berkeupayaan tinggi akan mengalami kemerosotan apabila karbon monoksida (CO) yang terkumpul memenuhi ruang aktif yang sepatutnya dimiliki oleh molekul hidrogen. Penyelidikan ini memfokuskan kepada penggunaan membran penukaran proton sel bahan api sebagai penukar elekrokimia CO. Konsep berbalik sel bahan api digunakan untuk menukarkan CO kepada karbon dioksida (CO_2) untuk mencapai kepekatan toleransi CO. Penukar elekrokimia CO menjalani tindak balas elektrokimia peralihan gas air (EWGSR) untuk menukarkan CO kepada CO_2. Lima sampel pemasangan membran elektrod (MEA) dengan nisbah yang berbeza daripada platinum (Pt) kepada paladium (Pd) pada karbon teraktif yang dilekatkan pada permukaan membran polibenzimidazol (PBI) disediakan. Sampel Pt-Pd/Ac MEA adalah dalam julat 1:0 kepada 1:4 yang mana mewakili nisbah Pt:Pd. Kesemua sampel diuji menggunakan gas hidrogen (CO/H_2) yang mengandungi 100 ppm CO. Membran PBI telah digunakan sebagai penukar elektrokimia CO kerana ia lebih murah dan boleh menerima CO tanpa perlu mengawal kandungan kelembapan. Parameter yang terlibat dalam proses penukaran elektrokimia CO adalah kadar alir CO/H_2, voltan bekalan kuasa dan suhu operasi. Prestasi penukaran karbon monoksida meningkat pada tiga keadaan pengoperasian, iaitu kadar alir gas CO/H_2 ialah 50 ml/min dengan voltan 0.7V pada suhu bilik. Keputusan yang didapati ialah 96.73% penukaran CO.

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LIST OF ABBREVIATIONS

FC	-	Fuel cell
PEM-FC	-	Polymer electrolyte membrane fuel cell or proton exchange membrane fuel cell
LT-PEMFC	-	Low temperature proton exchange membrane fuel cell
HT-PEMFC	-	High temperature proton exchange membrane fuel cell
CO	-	Carbon monoxide
CO_2	-	Carbon dioxide
H_2	-	Hydrogen gas
H_3PO_4	-	Phosphoric acid
H_2SO_4	-	Sulfuric acid
MEA	-	Membrane electrode assembly
GDL	-	Gas diffusion layer
PBI	-	Polybenzimidazole
SEM	-	Scanning electron microscope
FTIR	-	Fourier transform infrared spectroscopy
fcc	-	Face-centered cubic
XRD	-	X-ray diffraction
BET	-	Brunauer-Emmett-Teller
Pt	-	Platinum
Pd	-	Palladium
EWGS		Electrochemical water gas shift
EWGSR	-	Electrochemical water gas shift reaction

Ac	-	Activated carbon
M	-	Molarity
EIS	-	Electrochemical impedance spectroscopy
FRA	-	Frequency response analysis
Rs	-	Solution resistance
Rp	-	Polarization resistance
Rct	-	Charge transfer resistance
CPE	-	Constant phase element

LIST OF SYMBOLS

% - Percentage
n - Concentration
° - Degree
θ - Theta

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

There are many of the researchers all around the world working on clean and renewable sources of energy in reducing the dependence upon fossil fuels as the energy source to meet the demand from the consumers. In order to fulfill the demand, hydrogen has been identified as a potential alternative energy source where it is an energy carrier or a medium of storing or transporting energy with potential for extensive use in electricity generation for the industrial, commercial, residential, institutional, agricultural, and transportation. Furthermore, hydrogen contains almost three times the energy contained in natural gas (Amoo and Fagbenle, 2014). Due to the huge potential of hydrogen as the alternative fuel, a few methods have been found that can generate the hydrogen and these methods are thermochemical, electrochemical, photobiological and photoelectrochemical. One of the methods is thermochemical, it consists of several techniques to produce the hydrogen which are autothermal reforming, steam reforming, and gasification process, which can be applied to natural gas, coal or biomass to produce the hydrogen fuel. However, the hydrogen fuel that is produced from these methods is of low purity and need to undergo the purification process (Chen *et al*., 2008).

One of the technologies that can transform the hydrogen into a useful energy is the fuel cell where it converts directly the hydrogen into electricity. The function of the fuel cell system is to convert the chemical energy into the electrical energy, where it is a single step process to generate the electrical energy which by the reaction of reactants that takes place on the surface of the catalyst from the fuel cell. The fuel cell system can continuously generate the electrical energy as long as the reactants are kept on feeding into the system. The concept of fuel cell is similar to normal batteries, where it consists of electrolyte, cathode and anode electrodes, which undergo the electrochemical process, but the main advantage is that the reactants are supplied continuously. The reactants fed into the system are hydrogen and oxygen gas, where the hydrogen gas is fed through the anode and oxygen through the cathode. Throughout the system, the hydrogen is oxidized at the anode and oxygen is reduced at the cathode, as the hydrogen is oxidized, it does separate the electrons and protons where the protons are passed through the external circuit to generate electrical energy (Chandan *et al*., 2013).

There are a few types of fuel cell have been developed based on different types of electrolyte used. The electrolyte can be in the solid or liquid form. Each type of fuel cell has their capability and specialty. However, proton exchange membrane fuel cells, also known as polymer electrolyte membrane fuel cells (PEM-FC) is the most promising one as it has many advantages, among others, their advantages are low operating temperature, fast start-up, and high-power density (Mu *et al*., 2010). Therefore, PEM-FC has been widely used as a power generator and applied for portable, stationary and transportation system (Kim and Kim, 2012). Besides that, the hydrogen gas is one of the important components for the bright future of PEM-FC where a high purity of hydrogen gas is demanded in order to optimize the performance of PEM-FC in generating the electrical energy. From the total of hydrogen produced today, 96 percent comes from the steam reforming of fossil fuels (Busby, 2005)

The PEM-FC has been known as one of the leading green technologies as it only produces water as the side product when using hydrogen and oxygen as the raw materials (Zhang *et al.*, 2006). The water molecule is produced as the proton from the hydrogen gas passes through the membrane of the fuel cell to react with the oxidized oxygen at the cathode side. A high purity of hydrogen gas logically possesses a small amount of impurities and causes no defect on PEM-FC performance. However, from the previous study, they found out that some of the impurities can give a bad impact on the production of electrical energy from the PEM-FC itself. Most of the researchers focus on the presence of carbon monoxide (CO) molecules from the hydrogen-rich gas which believed can cause the conflict to fight on the active site of catalyst surface of the PEM-FC which is actually reserved for the hydrogen molecules to adsorb on it. The concentration of CO in hydrogen gas has to be reduced to a level below 20 ppm in order to avoid poisoning of the catalyst at the fuel cell electrodes (Galvita and Sundmacher, 2007).

There are two types of membrane film that are widely studied for fuel cell application, which are the Nafion and polybenzimidazole (PBI). The nafion membrane is commonly being used for low temperature PEM fuel cells (LT-PEMFCs) as the operating temperature can never be above 80°C in order to control the humidity losses to preserve the performance. While for the PBI membrane, this is one of the alternatives in order to encounter the carbon monoxide poisonous cases, where the PEM-FC can tolerate much more of the carbon monoxide concentration at high temperatures compared with the temperature that PEM-FC is being operated normally. The PBI membrane can tolerate a much higher operating condition temperature compared to nafion membrane which can go up to 200°C (Aili *et al.*, 2011). As the conventional PEM-FC is normally operated at 80°C, at this temperature the carbon monoxide content is as low as 10-20 ppm can cause the performance degradation where the carbon monoxide poisons the electrode platinum catalyst at the anode side which is where the hydrogen stream flows in (Das *et al.*, 2009).

The CO poisoning is a crucial problem which needs to be prevented in order to prolong the life span and to optimize and maintain the performance of the PEM-FC. In order to use the low purity of hydrogen which is from the reformer or other processes as the feedstock of PEM-FC, there is a need to have a hydrogen treatment process at a low level. This study proposes the electrochemical CO converter which undergoes the electrochemical water gas shift reaction (EWGSR) which was modified from PEM-FC to purify the low purity of hydrogen gas. This EWGSR can convert the poisonous CO into carbon dioxide (CO_2) and indirectly increase the yield of hydrogen gas at the cathode side of electrochemical CO converter (Giunta *et al.*, 2007).

1.2 Problem Statements

To optimize the generation of electrical energy from LT-PEMFCs at 80°C operating condition, a high purity of hydrogen has to feed to the anode of the system. However, a high purity hydrogen gas significantly affects the operating cost. A low purity hydrogen gas is suggested to be used as an alternative to lower the costing operation. This low purity hydrogen gas contains CO which can cause the performance degradation of LT-PEMFCs. The presence of 10-20 ppm of CO in hydrogen gas can contaminate the catalyst surface at the fuel cell electrode and degrade the performance of LT-PEMFCs (Das *et al.*, 2009). In order to provide a high purity of hydrogen gas to feed the LT-PEMFCs, the low purity of hydrogen gas needs to undergo the purification process. Besides the purity as one of the high costing factors, the metal that is used as the catalyst at the electrode also plays an important role.

The best electrocatalyst for both anode and cathode of PEM-FC is the platinum (Pt), where it has a high exchange current density for oxygen-reduction, a high resistance to chemical attack, excellent high-temperature characteristics, and stable electrical properties. However, Pt is expensive and the world's supply of Pt is limited and already in demand for other applications. As to promote low cost conditions, the Pt-alloy is proposed to reduce the requirement of Pt (Thanasilp and Hunsom, 2011). Besides that, the Pt based catalyst can be improved by alloying Pt with the nobel and non-nobel metals to tolerate CO and Pt-Ru is one of the most CO tolerant Pt based hydrogen oxidation catalysts (Modestov *et al.*, 2011). The palladium (Pd) can be found in the Earth's crust compared with the Pt which is limited makes the price of Pd is less expensive (Grigoriev *et al.*, 2007). The Pd is believed can partially replace the Pt as to create an alloy that can adsorb the CO in order to separate the CO from hydrogen gas (Chen *et al.*, 2012).

Other than that, the membrane that is commonly used for PEM-FC is Nafion and polybenzimidazole (PBI) membrane. The membrane applications also contribute to the high cost operation of fuel cell (FC). The PBI membrane is considerably cheaper compared to the nafion membrane (Kongstein et al., 2007). The PBI membranes need to treat with phosphoric acid (H_3PO_4) as to improve the proton conductivity. Phosphoric acid doped polybenzimidazole (H_3PO_4/PBI) is a successful membrane system that possesses excellent thermo-chemical stability and mechanical properties and good proton conductivity when doped with H_3PO_4 at elevated temperature (200°C) (Zhai *et al.*, 2007).

This study proposes the electrochemical water gas shift reaction (EWGSR) to convert the CO into CO_2 using the electrochemical CO converter which is modified from PEM-FC as a low level hydrogen gas purification system before the gas feed to a LT-PEMFCs. In addition, the electrochemical CO converter uses the Pt-Pd alloy as the electrocatalyst and H_3PO_4/PBI as the membrane of electrochemical CO converter. Huang *et al.*, (2006) also studied the EWGSR which was modified from PEM-FC to convert CO to CO_2. However, with Pt as the electrocatalyst and Nafion as the membrane at room temperature without elevating any operating conditions.

Oettel *et al.*, (2012) used the EWGSR to study the combined generation and separation of hydrogen using H_3PO_4/PBI membrane as the electrolyte and Pt or PtRu as the electrocatalyst at operating temperatures of 130°C and 150°C. This study aims to improve on the materials used as it affects the operating cost, where the use of PBI membrane and Pt-Pd alloy is because it is cheaper by reducing the consumption of Pt. Other than that, the operating conditions are manipulated as to optimize the performance of the reactor.

1.3 Research Objective

Based on the background of the study and the problem statement addressed, the objective of this study is to purify the hydrogen by converting the carbon monoxide (CO) presence from hydrogen-rich gas into carbon dioxide (CO_2) by the electrochemical water gas shift reaction (EWGSR) process from electrochemical CO converter which is modified from PEM fuel cell, which can be detailed as:

i. To obtain the best treatment condition for phosphoric acid doped PBI membrane for this system

ii. To find the best anode catalyst ratio between Pt and Pd

iii. To investigate the effect of operating parameters on conversion of CO such as flow rate of CO/H_2 gas, voltage supplied, and operating temperature

1.4 Research Scope

In order to achieve the objective of the research described in section 1.3, the following scopes are defined:

i. The treatment of the polybenzimidazole (PBI) membrane in phosphoric acid (H_3PO_4) solution using two different acid conditions such as soaked into 85 wt.% H_3PO_4 for 14 days and soaked in 5 M H_3PO_4 for 3.5 hours at 80°C.

ii. The characterization of polybenzimidazole (PBI) membrane was analyzed by using the electrochemical impedance spectroscopy (EIS) and the fourier transform infrared spectroscopy (FTIR) analyzer.

iii. The preparation of anode catalyst by varying the ratio (1:0), (1:1), (1:2), (1:3) and (1:4) between platinum (Pt) and palladium (Pd) with 20 wt. % of total metal.

iv. The characteristics of anode catalyst surface preparation is observed by using the scanning electron microscopy (SEM), x-ray diffraction (XRD) and Brunauer, Emmett and Teller (BET).

v. The operating parameter evaluation such as, flow rate of CO/H_2 gas (50-150 sccm), voltage supplied (0.6-0.8V) and temperature (28°C-200°C) towards the removal of carbon monoxide. The CO analyzer was used for measurement.

1.5 Significant of Study

Nafion based membrane fuel cells operate at its best at 80 °C to generate electrical energy with pure hydrogen used as the anode feed gas (Boaventura and Mendes, 2010). A carbon monoxide removal system which is electrochemical CO converter based on the EWGSR is proposed in order to use industrial-grade hydrogen gas for PEM-FC to generate the electrical energy. The existence of electrochemical CO converter as the CO removal system can reduce the cost by generating electrical energy as the high purity of hydrogen is much more expensive. This electrochemical CO converter can be used for on board or off board because the operating temperature can be both high and low due to the use of PBI membrane as the electrolyte. This system also can be applied as the purification system for the recycle stream from the exhaust gas from the fuel cell. This study can be one of the references for future research because of the never ending poisonous effect of CO towards the fuel cell performance. The study on reducing the CO concentration from hydrogen-rich gas is still valid as the application of fuel cell technology is developing rapidly.

1.6 Thesis Outline

This thesis is divided into five chapters; where the chapter 1 covers the background, problem statement, objective, scope and significance of the study as to lead towards the aims of the research in which to reduce the carbon monoxide content from hydrogen-rich gas to a tolerable value. The literature review is discussed in the chapter 2, findings from the previous research are included in the current knowledge for both theory and methodology based upon the title of the thesis. While for chapter 3, it is about the methodology which involves the method on catalyst preparation, sample assembles, summary of research and experimental flow diagram. The discussion about the results obtained from a series of experiment is presented in chapter 4 and chapter 5 is the conclusion from the finding of the research study and some recommendations for the improvement of the research interest.

REFERENCES

Aili, D., Hansen, M. K., Pan, C., Li, Q., Christensen. E., Jensen, J. O., and Bjerrum, N. J. (2011). Phosphoric acid doped membranes based on Nafion®, PBI and their blends - Membrane preparation, characterization and steam electrolysis testing. *International Journal of Hydrogen Energy*. 36(12), 6985–6993.

Aktas, S., and Morcali, M.H. (2011). Platinum recovery from dilute platinum solutions using activated carbon. *Transactions of Nonferrous Metals Society of China (English Edition)*. 21(11), 2554–2558.

Al-Madani, G., Kailani, M. H. and Al-Hussein, M. (2015). Test system for through-plane conductivity measurements of hydrogen proton exchange membranes. *International Journal of Electrochemical Science*. 10(8), 6465–6474.

Amoo, L. and Fagbenle, R. L. (2014). An integrated impact assessment of hydrogen as a future energy carrier in Nigeria's transportation, energy and power sectors. *International Journal of Hydrogen Energy*. 39, 12409-12433.

Barbir, F. (2013). *PEM fuel cells, theory and practice*. (2nd edition). Academic Press: Elsevier Inc.

Belvedere, B., Bianchi, M., Borghetti, A., Pascale, A. D., Paolone, M. and Vecci, R. (2013). Experimental analysis of a PEM fuel cell performance at variable load with anodic exhaust management optimization. *International Journal of Hydrogen Energy*. 38, 385-393.

Boaventura, M., and Mendes, A. (2010). Activation procedures characterization of MEA based on phosphoric acid doped PBI membranes. *International Journal of Hydrogen Energy*. 35(20), 11649–11660.

Bouchet, R., and Siebert, E. (1999). Proton conduction in acid doped polybenzimidazole. *Solid State Ionics*. 118, 287–299.

Bouchet, R., Miller, S., Duclot, M., and Souquet, J. L. (2001). A thermodynamicapproach to proton conductivity in acid-doped polybenzimidazole. *Solid State Ionics.* 145(1-4), 69–78.

Bruno, M. M., Franceschini, E. A., Viva, F. A., Thomas, Y. R. J., and Corti, H. R. (2012). Electrodeposited mesoporous platinum catalysts over hierarchical carbon monolithic support as anode in small PEM fuel cells. *International Journal of Hydrogen Energy*. 37(19), 14911–14919.

Busby, R. L. (2005). *Hydrogen and fuel cells a comprehensive guide*. (1st edition). Oklahoma: Penn Well Corporation.

Chandan, A., Hattenberger, M., El-kharouf, A., Du, S., Dhir, A., Self, V., Pollet, B. G., Ingram, A. and Bujalski, W. (2013). High temperature (HT) polymer electrolyte membrane fuel cells (PEMFC)-A review. *Journal of Power Sources*. 231, 264-278.

Chen, W. H., Hsieh, T. C. and Jiang, T. L. (2008). An experimental study on carbon monoxide conversion and hydrogen generation from water gas shift reaction. *Energy Conversion and Management*. 49, 2801-2808.

Chen, M. L., Park, C. Y., Choi, J. G., and Oh, W. C. (2011). Synthesis and characterization of metal (Pt, Pd and Fe)-graphene composites. *Journal of the Korean Ceramic Society*. 48(2), 147–151.

Chen, R., Chen, Z., Ma, B., Hao, X., Kapur, N., Hyun, J., Cho, K. and Shan, B. (2012). CO adsorption on Pt (111) and Pd (111) surfaces: A first-principles based lattice gas Monte-Carlo study. *Computational and Theoretical Chemistry*. 987, 77-83.

Chen, W. C., Tsai, D. S., Tseng, L. W., Yang, L. R. and Le, M. V (2014). Proton exchange membrane fuel cell of polybenzimidazole electrolyte doped with phosphoric acid and antimony chloride. *International Journal of Hydrogen Energy*. 39, 10245-10252.

Das, S. K., Reis, A. and Berry, K. J. (2009). Experimental evaluation of CO poisoning on the performance of a high temperature proton exchange membrane fuel cell. *Journal of Power Sources*. 193, 691-698.

Doucet, R., Gardner, C. L. and Ternan, M. (2009). Separation of hydrogen from hydrogen/ethylene mixtures using PEM fuel cell technology. *International Journal of Hydrogen Energy*. 34, 998-1007.

Eisman, G. A., McElroy, J. F. and Peschke, N. (2001). *United States Patent 6,280,865 B1*. Retrieved on September 19, 2013, from http://www.patentlens.net/

El-Shafey, E. I., Ali, S. N. F., Al-Busafi, S., and Al-Lawati, H. A. J. (2016). Preparation and characterization of surface functionalized activated carbons from date palm leaflets and application for methylene blue removal. *Journal of Environmental Chemical Engineering*. 4, 2713–2724.

Fermoso, J., He, L. and Chen, D. (2012). Production of high purity hydrogen by adsorption enhanced steam reforming of crude glycerol. *International journal of hydrogen energy*. 37, 14047-14054.Galvita, V. and Sundmacher, K. (2007). Cyclic water gas shift reactor (CWGS) for carbon monoxide removal from hydrogen feed gas for PEM fuel cells. *Chemical Engineering Journal*. 134, 168-174.

Galvita, V. and Sundmacher, K. (2007). Cyclic water gas shift reactor (CWGS) for carbon monoxide removal from hydrogen feed gas for PEM fuel cells. *Chemical Engineering Journal*. 134, 168-174.

Gardner, C. L. and Ternan, M. (2007). Electrochemical separation of hydrogen from reformate using PEM fuel cell technology. *Journal of Power Sources*. 171, 835-841.

Geng, Z., Wang, D., Zhang, C., Zhou, X., Xin, H., Liu, X., and Cai, M. (2014). Spillover enhanced hydrogen uptake of Pt/Pd doped corncob-derived activated carbon with ultra-high surface area at high pressure. *International Journal of Hydrogen Energy*. 39(25), 13643–13649.

Giunta, P., Mosguera, C., Amadeo, N. and Laborde, M. (2007). Simulation of a hydrogen production and purification system for a PEM fuel cell using bioethanol as raw material. *Journal of Power Sources*. 164, 336-343.

Glipa, X., Bonnet, B., Mula, B., Jones, D. J., and Roziere, J. (1999). Investigation of the conduction properties of phosphoric and sulfuric acid doped polybenzimidazole. *Journal of Materials Chemistry*. 9(12), 3045–3049.

Gourdoupi, N., Kallitsis, J. K. and Neophytides, S. (2010). New proton conducting polymer blends and their fuel cell performance. *Journal of Power Sources*. 195, 170-174.

Grabow, L. C., Gokhale, A. A., Evans, S. T., Dumesic, J. A., and Mavrikakis, M. (2008). Mechanism of the water gas shift reaction on Pt: First principles, experiments, and microkinetic modeling. *Journal of Physical Chemistry C*. 112(12), 4608–4617.

Grigoriev, S. A., Lyutikova, E. K., Martemianov, S. and Fateev, V. N. (2007). On the possibility of replacement of Pt by Pd in a hydrogen electrode of PEM fuel cells. *International Journal of Hydrogen Energy*. 32, 4438-4442.

Gudarzi, D., Ratchananusorn, W., Turunen, I., Heinonen, M., and Salmi, T. (2015). Factors affecting catalytic destruction of H2O2 by hydrogenation and decomposition over Pd catalysts supported on activated carbon cloth (ACC). *Catalysis Today*. 248, 69–79.

He, R., Li, Q., Xiao, G., and Bjerrum, N. J. (2003). Proton conductivity of phosphoric acid doped polybenzimidazole and its composites with inorganic proton conductors. *Journal of Membrane Science*. 226(1-2), 169–184.

Hetland, J. and Mulder, G. (2007). In search of a sustainable hydrogen economy: How a large-scale transition to hydrogen may affect the primary energy demand and greenhouse gas emissions. *International Journal of Hydrogen Energy*. 32, 736-737.

Hocevar, S. and Summers, W. (2008). *Hydrogen cycle: Hydrogen production*. Leon, A. *Hydrogen Technology Mobile and Portable Applications*. (pp. 15-30). Germany: Springer-Verlag.

Hogarth, W. H. J. and Benziger, J. B. (2006). Operation of polymer electrolyte membrane fuel cells with dry feeds: design and operating strategies. *Journal of Power Sources*. 159, 968-978.

Huang, C., Jiang, R., Elbaccouch, M., Muradov, N. and Fenton, J. M. (2006). On-board removal of CO and other impurities in hydrogen for PEM fuel cell applications. *Journal of Power Sources*. 162-563-571.

Hwang, K., Kim, J. H., Kim, S. Y., and Byun, H. (2014). Preparation of polybenzimidazole-based membranes and their potential applications in the fuel cell system. *Energies*. 7(3), 1721–1732.

Jeong, Y. H., Jung, J. H., Choi, E., Han, S., Begley, A. I., Yoo, S. J., Jang, J. H., Kim, H. J., Nam, S. W., Lee, K. Y., and Kim, J. Y. (2015). Colorimetric determination of phosphoric acid leakage for phosphoric acid-doped polybenzimidazole membrane fuel cell applications. *Journal of Power Sources*. 299, 480–484.

Jensen, J. O. and Li, Q. (2008). *Hydrogen cycle: Fuel cells*. Leon, A. *Hydrogen Technology Mobile and Portable Application*. (pp 151-175). Germany: Springer-Verlag.

Kim, B. J. and Kim, S. K. (2012). Studies on the cathode humidification by exhaust gas recirculation for PEM fuel cell. *International Journal of Hydrogen Energy*. 37, 4290-4299.

Kongstein, O. E., Berning, T., Borresen, B., Seland, F. and Tunold, R. (2007). Polymer electrolyte fuel cells based on phosphoric acid doped polybenzimidazole (PBI) membranes. *Energy*. 32, 418-422.

Korotkikh, O. and Farrauto, R. (2000). Selective catalytic oxidation of CO in H_2: fuel cell applications. *Catalysis Today*. 62, 249-254.

Lee, H. J., Lee, D. H., Henkensmeier, D., Jang, J. H., Cho, E. A., Kim, H. J., and Kim, H. (2012). Synthesis and Characterization of H 3 PO 4 Doped Poly(benzimidazole-co-benzoxazole) Membranes for High Temperature Polymer Electrolyte Fuel Cells. *Bulletin of the Korean Chemical Society*. 33(10), 3279–3284.

Leon, A. (2008). *Hydrogen cycle: Introduction*. Leon, A. *Hydrogen Technology Mobile and Applications*. (pp. 1-13). Germany: Springer-Verlag.

Li, H., Lee, K. and Zhang, J. (2008). *Electrolysis H_2 oxidation reaction*. Zhang, J. *PEM fuel cell electrocatalyst and catalyst layers*. (pp 1-20). Canada: Springer-Verlag.

Li, Q., Jensen, J. O., Savinell, R. F., and Bjerrum, N. J. (2009). High temperature proton exchange membranes based on polybenzimidazoles for fuel cells. *Progress in Polymer Science*. 34(5), 449–477.

Lopes, T., Antolini, E., and Gonzalez, E. R. (2008). Carbon supported Pt-Pd alloy as an ethanol tolerant oxygen reduction electrocatalyst for direct ethanol fuel cells. *International Journal of Hydrogen Energy*. 33(20), 5563–5570.

Mamlouk, M. and Scott, K. (2010). The effect of electrode parameters on performance of phosphoric acid-doped PBI membrane fuel cell. *International Journal of Hydrogen Energy*. 35, 784-793.

Mamlouk, M., and Scott, K. (2011). Analysis of high temperature polymer electrolyte membrane fuel cell electrodes using electrochemical impedance spectroscopy. *Electrochimica Acta*. 56(16), 5493–5512.

Modestov, A. D., Tarasevich, M. R. and Leykin, A. Y. (2011). CO electrooxidation study on PT and Pt-Ru in H3PO4 using MEA with PBI-H3PO4 membrane. *Journal of Power Sources*. 196, 2994-3002.

Mu, S., Zhao, P., Xu, C., Gao, Y. and Pan, M. (2010). Detaching behaviors of catalyst layers applied in PEM fuel cells by off-line accelerated test. *International Journal of Hydrogen Energy*. 35, 8155-8160.

Nachiappan, N. and Kalaignan, G. P. (2013). Effect of nitrogen and carbon dioxide as fuel impurities on PEM fuel cell performances. *Department of Chemical Engineering*. 19, 251-354.

Oettel, C., Struckmann, L. R. and Sundmacher, K. (2012). Combined generation and separation of hydrogen in an electrochemical water gas shift reactor (EWGSR). *International Journal of Hydrogen Energy*. 37, 6635-6645.

Oettel, C., Struckmann, L. R. and Sundmacher, K. (2012). Characterization of the electrochemical water gas shift reactor (EWGSR) operated with hydrogen and carbon monoxide rich feed gas. *International Journal of Hydrogen Energy*. 37, 11759-11771.

Oono, Y., Sounai, A., and Hori, M. (2009). Influence of the phosphoric acid-doping level in a polybenzimidazole membrane on the cell performance of high-temperature proton exchange membrane fuel cells. *Journal of Power Sources*. 189(2), 943–949.

Othman, R., Dicks, A. L. and Zhu, Z. (2012). Non precious metal catalyst for the PEM fuel cell cathode. *International Journal of Hydrogen Energy*. 37, 357-372.

Pak, S. H., Jeon, M. J., and Jeon, Y. W. (2016). Study of sulfuric acid treatment of activated carbon used to enhance mixed VOC removal. *International Biodeterioration and Biodegradation*. 113 195–200.

Perry, K. A., Eisman, G. A. and Benicewicz, B. C. (2008). Electrochemical hydrogen pumping using a high-temperature polybensimidazole (PBI) membrane. *Journal of Power Sources*. 177, 478-484.

Qi, Z., and Buelte, S. (2006). Effect of open circuit voltage on performance and degradation of high temperature PBI-H3PO4 fuel cells. *Journal of Power*

Sources. 161(2), 1126–1132.

Qingfeng, L., Hjuler, H. A. snd Bjerrum, N. J. (2001). Phosphoric acid doped polybenzimidazole membranes: physiochemical characterization and fuel cell applications. Journal of Applied Electrochemistry. 31, 773-779.

Singh, S., and Verma, N. (2015). Fabrication of Ni nanoparticles-dispersed carbon micro-nanofibers as the electrodes of a microbial fuel cell for bio-energy production. *International Journal of Hydrogen Energy*. 40(2), 1145–1153.

Smith, R. A. (2004). *Hydrogen purity standard*. Compress Gas association.

Sorensen, B. (2005). *Hydrogen and fuel cells*. (1st edition). Elsevier Academic Press: Elsevier Inc.

Srinivasan, S. and Ogden, J. (2006). *Fuels: Processing, storage, transmission, distribution, and safety*. Srinivasan, S. *Fuel cells from fundamentals to applications*. (pp. 375-385). New York: Springer science + Business Media, LLC.

Srinivasan, S. (2006). *Evolution of electrochemistry*. Srinivasan, S. *Fuel cells from fundamentals to applications*. (pp. 3-14). New York: Springer science + Business Media, LLC.

Srinivasan, S. Krishnan, L. and Marozzi, C. (2006). *Fuels cell principles*. Srinivasan, S. *Fuel cells from fundamentals to applications*. (pp. 189-199). New York: Springer science + Business Media, LLC.

Srinivasan, S. and Kirby, B. (2006). *Status of fuel cell technology*. Srinivasan, S. *Fuel cells from fundamentals to applications*. (pp. 441-446). New York: Springer science + Business Media, LLC.

Takenaka, S., Shimizu, T. and Otsuka, K. (2004). Complete removal of carbon monoxide in hydrogen-rich gas stream through methanation over supported metal catalysts. *International Journal of Hydrogen Energy*. 29, 272-284.

Termpornvithit, C., Chewasatn, N. and Hunsom, M. (2012). Stability of Pt-Co/C and Pt-Pd/C based oxygen reduction reaction electrocatalysts prepared at a low temperature by a combined impregnation and seeding process in PEM fuel cells. *J Appl Electrochem*. 42, 169-178.

Thanasilp, S., and Hunsom, M. (2011). Effect of Pt: Pd atomic ratio in Pt-Pd/C electrocatalyst-coated membrane on the electrocatalytic activity of ORR in PEM fuel cells. *Renewable Energy*. 36(6), 1795–1801.

Thanasilp, S. and Hunsom, M. (2011). Preparation of a high-performance Pt-Pd/C-electrocatalyst-coated membrane of ORR in PEM fuel cells via a combined process of impregnation and seeding: effect of electrocatalyst loading on carbon support. *Electrochimica Acta*. 56, 1164-1171.

Todoroki, N., Osano, H., Maeyama, T., Yoshida, H. and Wadayama, T. (2009). Infrared reflectrion absorption spectral study for CO adsorption on Pd/Pt(111) bimetallic surfaces. *Applied Surface Science*. 256, 943-947.

Wang, C. P., Chu, H. S., Yan, Y. Y. and Hsueh, K. L. (2007). Transient evolution of carbon monoxide poisoning effect of PBI membrane fuel cells. *Journal of Power Sources*. 170, 235-241.

Wang, H. and Yuan, X. Z. (2008). *PEM fuel cell fundamentals*. Zhang, J. *PEM fuel cell electrocatalyst and catalyst layers*. (pp. 1-20). Canada: Springer-Verlag.

Wojnicki, M., (2013). Adsorption and reduction of platinum(IV) chloride complex ions on activated carbon. *Transactions of Nonferrous Metals Society of China (English Edition)*. 23(4), 1147–1156.

Yao, S., Zhang, J., Shen, D., Xiao, R., Zhao, M., and Liang, J. (2016). Removal of Pb(II) from water by the activated carbon modified by nitric acid under microwave heating. *Journal of Colloid and Interface Science*. 463, 118–127.

Zamel, N. and Li, X. (2011). Effect of contaminations on polymer electrolyte membrane fuel cells. *Progress in Energy and Combustion Science*. 37, 292-329.

Zeis, R. (2015). Materials and characterization techniques for high-temperature polymer electrolyte membrane fuel cells. *Beilstein Journal of Nanotechnology*. 6(1), 68–83.

Zhai, Y., Zhang, H., Zhang, Y. and Xing, D. (2007). A novel H_3PO_4/Nafion-PBI composite membrane for enhanced durability of high temperature PEM fuel cells. *Journal of Power Sources*. 169, 259-264.

Zhai, Y., Zhang, H., Xing, D. and Shao, Z. G. (2007). The stability of Pt/C catalyst in H3PO4/PBI PEMFC during high temperature life test. *Journal of Power Sources*. 164, 126-133.

Zhang, H., (2004). Synthesis , Characterization and Fuel Cell Performance of Poly (2 , 2 ’ - (P-Phenylene) - Temperature Fuel Cell Membrane. *Fuel*. 49(2), 588–589.

Zhang, J., Xie, Z., Zhang, L., Tang, Y., Song, C., Navessin, T., Shi, Z., Song, D., Wang, H., Wilkinson, D. P., Liu, Z. S. and Holdcroft, S. (2006). High temperature PEM fuel cell. *Journal of Power Sources*. 160, 872-891.

Zhang, J., Tang, Y., Song, C. and Zhang, J. (2007). Polybenzimidazole-mmebrane-based PEM fuel cell in the temperature range of 120-200^{0}C. *Journal of Power Sources*. 172, 163-171.

Zhang, H., Wang, X., Zhang, J. and Zhang, J. (2008). *Conventional catalyst ink, catalyst layer and MEA preparation*. Zhang, J. *PEM fuel cell electrocatalyst and catalyst layers*. (pp 1-20). Canada: Springer-Verlag.