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Study on the Corrosion Resistance of Metal Bipolar-Plate of Fuel Cell

Chien-Ju Hung*, Chao-An Lin*, Wei-Jen Chen*, Huan-Ruei Shiu*and Bin-Hao Chen**

Keywords: fuel cell, metal bipolar plate, contact resistance, MEA porosity

ABSTRACT

The study probed the corrosion of metal bipolar plate of fuel cell caused by the reaction in the fuel cell flow channel, as the higher interface impedance contact with bipolar plate induced by corrosion during chemical reaction flow process of the plate discounts the performance of fuel cell significantly. Therefore, it is critical for fuel-cell performance to choose corrosion-resistant metal with low impedance, so as to attain effective contact with MEA and lower the contact-induced impedance. Via impact extrusion of metal flow channel and electrochemical-experiment analysis and measurement, the relationship between fuel cell performance and its structural features can be learned. Then, measure and analyze the impedance of metallic materials with different conductivity and emulate the features of the corrosive electric current of PEM fuel cell before observing the appearance of metallic material and measuring its impedance via measurement in experiment, thereby ascertaining the relationship between the metal's corrosion-resistance ability and the performance of fuel cell.

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**Engineering Building 1, No. 101, Section 2, Kuang-Fu Road, Hsinchu, Taiwan 30013, Department of Power Mechanical Engineering, National Tsing Hua University*

***No. 1, Sec. 3, Zhongxiao E. Rd., Taipei City 10608, Taiwan, R.O.C.*
Department of Vehicle Engineering, National Taipei University of Technology
Tel: +886-2-2771-2171 Ext. 3604
binhao17@gmail.com (Bin-Hao Chen)
(To whom correspondence and reprint requests should be addressed)

INTRODUCTION

Literature on structural design of PEM fuel cell

Literature and practical operation show that the metal bipolar plate of fuel cell stack is meant mainly for providing the fuel through the membrane diffusion, delivering cooling fluid to remove the heat generation by the reaction, separating fluid, discharging condensed water, inducing electric current, bolstering structure, and separating monocells, with its key features listed below:

First feature we considered is the electric conductivity. A Fuel cell with metal bipolar plate boasts better energy conersion efficiency, due to metal's superior conductivity than graphite or carbon-based materials. Metal's conductivity is about 5,000 times than that of common graphite. For instance, pure graphite cannot be used as fuel cell bipolar plate due to lower rigidity and stiffness, although its conductivity may be better than some metal materials. Another key features of metal bipolar plate should be mentioned is the acid corrosion resistance. As we know, acidity and corrosion resistance are indispensable for bipolar plate, given its acid operating environment under 2~3 pH value. As the acidity and corrosion resistance of most metals is not good, except some alloys like lead-, tin-, and aluminum-based. It needs, therefore, to plate or deposit acidity proof and corrosion-resistant material, such as Teflon, onto the surface of metal bipolar plate or candidate for metallic bipolar plate. Once the crack appears on the corrosion-resistant layer, the life cycle of metal plate will be decay.

In summary, lightweight fuel cell with metal bipolar plate is a candidate suited to vehicles, such as fuel cell car. Metal bipolar plate provide another choice can be for design according to the different applications of different application scenarios. Given the energy-market demand of durability and low cost (Tawfik et. al., 2007), metal bipolar plate with higher power density, higher mechanical strength, lower production cost, and mass-production feasibility has high commercialized value. Meanwhile, due to its lower rigidity, the development of fuel cell with metal bipolar plate has to overcome high technological threshold, which needs operating experiences and significant input. In view of its commercial and research value, current study will examine fuel-cell stack with metal bipolar plate and look into its corrosion caused by the flow channel. Literature Liu et. al.(2009) pointed to the effect of the error in the size of metal bipolar plate on the pressure distribution between the interface of the gas diffusion layer and the plate. Reference Liu et. al.(2009) conducted sensitivity analysis of pressure distribution on membrane electrodes of multiple fuel cells, with the result shown in Fig. 1. Kusoglu et. al. (2006) looked into the effect of fuel cell water and heat management; the hydro-thermal cycle, finding that restriction of the extension of fuel cell membrane electrode in its structural conditions may cause plastic deformation, such as locking of screw bolt. As fuel cell stops operation, driving down temperature, membrane electrode begins to contract and plastic deformation during operation generates residual stress. Repetition all of the cycles for thousands times would cause fatigue and failure in the multi-layered membrane electrode, resulting in the appearance of cracks and pores in the electrode. Literature Vlahinos et. al. (2006) proposed an optimal design for pad shape and flow-channel width to improve the sealing of bipolar plate and end plate. Lai et. al. (2007) presented a robust design featuring even pressure distribution, pointing out that the effect of fuel cell stack assembly pressure on the even distribution of membrane-electrode pressure is much greater than the position for the locking of screw bolt and presenting optimal assembly pressure and influence of the screw bolt-locking position.

As for bipolar design, literature Wang et. al. (2003) compared four different kinds of stainless steel, finding that stainless steel 349 performs better in contact electric resistance, due to higher content of chromium, which has an inverse relationship with the level of electric resistance, as shown in Fig. 2.

Greenwood et. al. (1966) put forth a mathematic model on contact electric resistance, while literature Mishra et. al. (2004) modified fractal theoretical model and employed it to estimate the contact electric resistance of gas diffusion layer and bipolar plate, with the result having been proven to be quite accurate, after comparison with experimental results, as shown in Fig. 3.

Literature Zhou et. al. (2006) simplified fractal theory and show the advantage of other scholars' experimental data to formulate relation between contact pressure and electrical resistivity.

$$\rho = A\left(\frac{B}{P}\right)^{c}$$

In which these three parameters in the formula; A, B, C are constants and vary along with change of material.

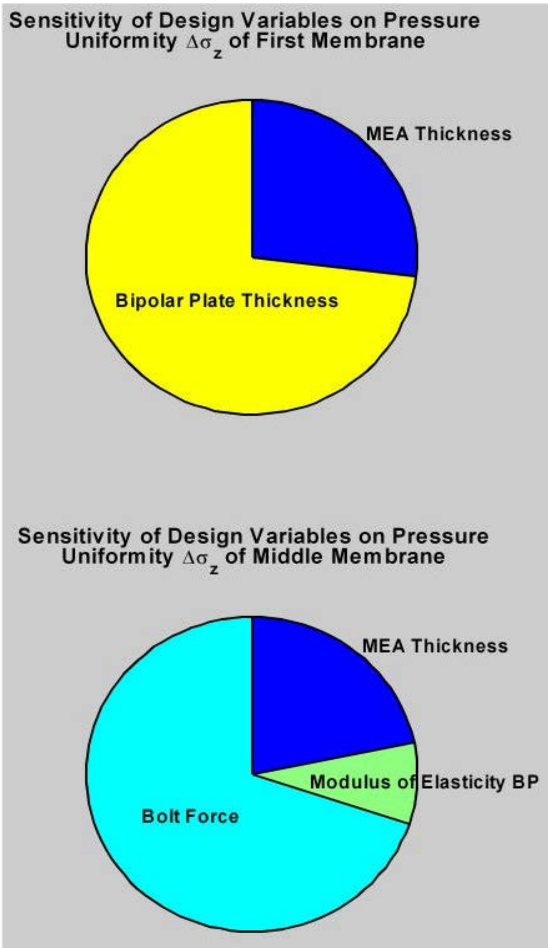

Fig. 1. Sensitivity analysis of the pressure distribution of multi-fuel cell set (Vlahinos et. al., 2003)

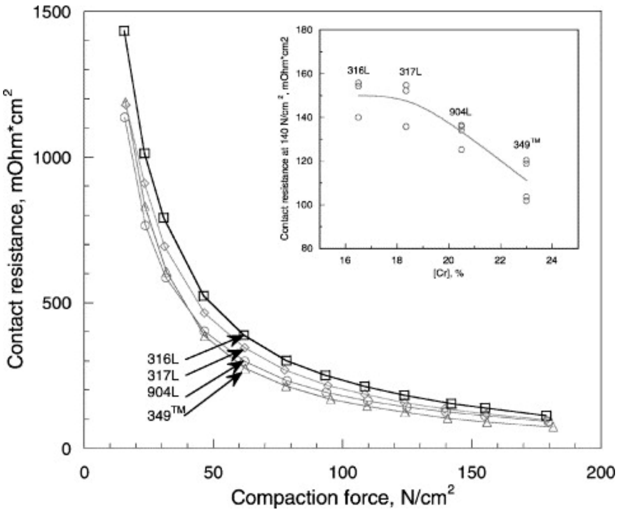

Fig. 2. Reaction of different kinds of stainless steel to contact electric resistance with different pressure, with the chromium contents of different kinds of stainless steel shown in the small inside figure. (Wang et. al., 2003)

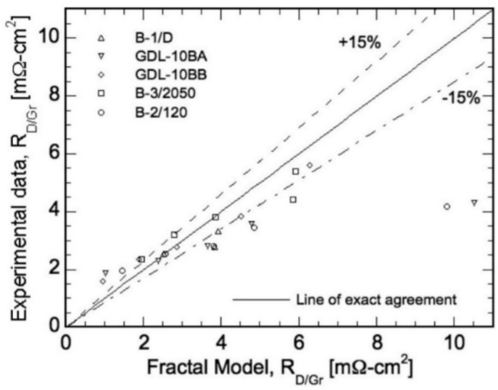

Fig. 3. Comparison of experiment of multiple GDL samples and contact pressure and the forecast value of fractal-theoretical model.

In which these three parameters in the formula; A, B, C are constants and vary along with change of material. Bipolar-plate flow channel in square shape performs better, according to the literature. Figure 4 shows the respective porosity distributions of square rib and semicircular rib, while Figure 5 manifests the effect of square rib and semicircular rib on contact electric resistance and porosity.

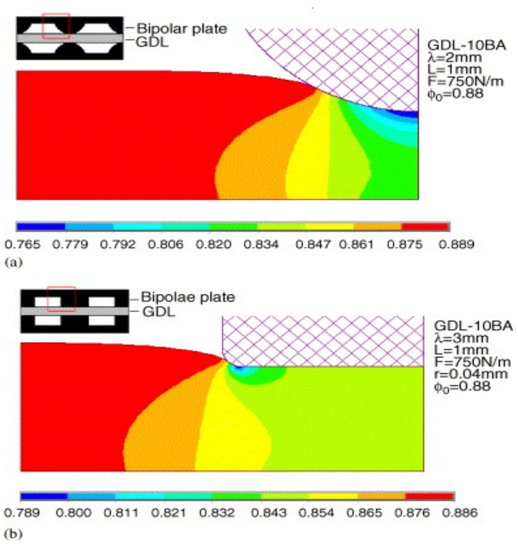

Fig. 4. Porosity distributions of square rib and semicircular rib (Zhou et. al., 2006)

Literature Zhang et. al. (2006) proposed the fractional modes of three different pressures and calculate their respective contact electric resistances, finding that contact electric resistance hinges on the scale of compression pressure, irrelevant to whether pressure is evenly distributed on the contact surface. Finally, Ihonen et. al. (2001) conducted several experiments to measure thin film-coated and pristine aluminum-alloy (316) metal bipolar plants in different compression pressure, gaseous pressure, and electric-current density, finding that film-coated metal bipolar plate has smaller contract electric resistance and is more stable.

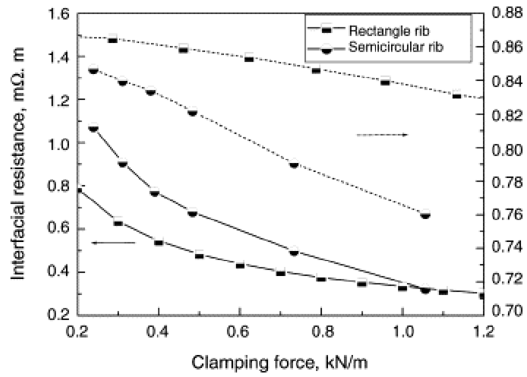

Fig. 5. Effect of square rib and semicircular rib on contact electric resistance and porosity (Zhou et. al., 2006)

METHODS

Experimental design

Given the nature and purpose of the study, the experiment employed potentiodynamic polarization method for corrosion-resistance analysis, frequency response analyzer Autolab with type No. PGSTAT20, as shown in Fig. 6, for polarization test, Ag/AgCl as reference electrode, and platinum as counter electrode, with 0.244V as standard reduction potential relative to standard hydrogen electrode (SHE), working electrode (WE) connected to test piece, and H_2SO_4 solution with pH=3 as the emulated operating environment for PEM (proton exchange membrane) fuel cell. In order to precisely control the concentration level of corrosive fluid in emulating the operating environment of PEM fuel cell and avoid external variables, such as oxygen content, affecting the stability of the polarization curve of electro kinetic potential resulting in distortion, deionized water was employed as solvent in preparing corrosive fluid. Using measuring glass to control the dosage of ingredients for deionized water and sulfuric solution before pouring ingredients in reactor tank and stirring them with magnet stirrer to increase the uniformity of fluid. Scanning speed was set at 5 mV/sec for a scope corresponding to open circuit potential (OCP) at -0.3 V-0.8 V. The polarization curve of test piece's electro kinetic potential could be obtained by recording the voltage and electric-current values during the experimental process.

In addition, metal materials with different conductivity were employed to measure and analyze their impedance and emulate the corrosive electric current of PEM fuel cell, via measurement and observation of the materials' appearance and impedance performance in experiment, so as to ascertain the relationship between their corrosion-resistance capability and performance. The experiment and analysis was carried out in four steps:

a. Measure the impedance of metal with good conductivity followed by verification with Milli-OHM meter and four-point probe;

b. emulate the corrosive electric current in the operation of PEM fuel cell and verify its corrosive status and electric current;

c. compare and analyze the corrosive electric current of stainless steel substrate and metal substrate with metal coating with good conductivity and corrosion-resistance;

d. compare and analyze the corrosive electric currents of red-copper substrate coated with nickel and chromium.

Via the four steps, the relationship between the corrosive electric currents of different metal substrates can be learned.

Fig. 6. Potentiostat AUTOLAB PGSTAT20

Verification of the impedance of metal substrates

A number of metal substrates were chosen, out of the consideration of price and availability, for measurement in the experiment, as shown in Fig. 7:

Fig. 7. Different metal substrates

The metal substrates, sized 2.5cm*2.5cm, were measured with Milli-OHM meter and four-point probe for their impedance, for use in subsequent verification and analysis in the experiment. Due to its good conductivity and less rebound in processing, as shown in impedance analysis, red copper substrate was selected and added with corrosion-resistance coating for the production a highly conductive and low-corrosion metal bipolar plate for testing in the experiment.

Verification of Metal bipolar plate corrosive status and electric current

Setup of chemical tank for solution in the emulation. Pour 0.0005M 300mL H_2SO_4 into a fixed-capacity container before addition of 0.1ppm NaF, as shown in Fig. 8.

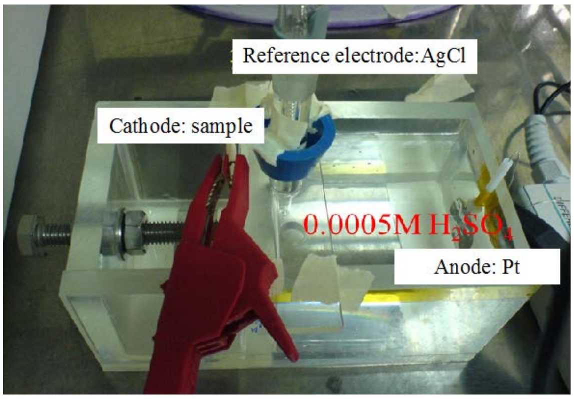

Fig. 8. Setup of corrosive environment for emulating operation of PEM fuel cell

Employ the emulated chemical tank in the quantitative test of the state of the corrosive electric current of metal substrate and emulate the function of metal substrate in the operation of PEM fuel cell to obtain the corrosive electric current against the different coating layers for analysis.

Analysis of the corrosive electric current of stainless-steel substrate

Given stainless-steel substrate's corrosion tolerance, two common stainless steels 316L and 304 were employed in the experiment for corrosion analysis before comparison with the corrosive electric current of other metal substrates with good conductivity but less corrosion resistance, as shown in Fig. 9, whose results can be used as reference for the selection of metal substrate and coating in the future. The experiment shows that stainless steels 304 and 316L outperform other metal substrates in corrosion resistance

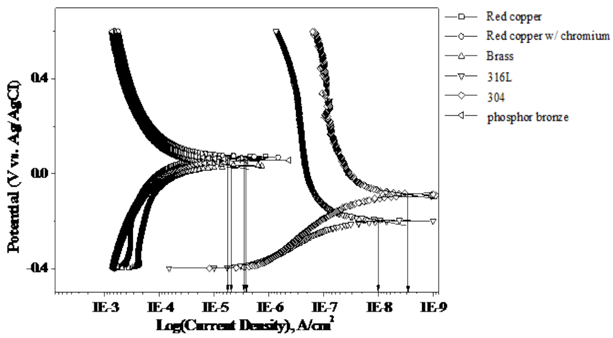

Fig. 9. Corrosion electric potentials of stainless steel substrate and other metal substrates

Comparative analysis of the corrosive electric currents of red copper substrate with nickel and chromium coatings

Despite the merits of good conductivity and low rebound in processing, red copper is not a good material for metal plate, due to low corrosion resistance. In the experiment, red copper is coated with nickel and chromium, both featuring good conductivity and corrosion resistance, in various modes and at various thickness for corrosion analysis, as well as comparison with stainless steel 316L, as shown in Fig. 10, whose results can be used as reference for different metal substrate coatings in the future.

Table 1. Thickness and conductivity of nickel-chromium-coatings for red-copper substrate

	Red copper	Red copper with one layer of nickel and chromium	Red copper with three layers of nickel and chromium
Thickness (mm)	0.20	40μm_Ni+ 0.25μm_Cr	45μm_Ni+ 0.25μm_Cr
Conductivity (s/cm)	$1.6*10^6$	$9.172*10^5$	$8.812*10^5$

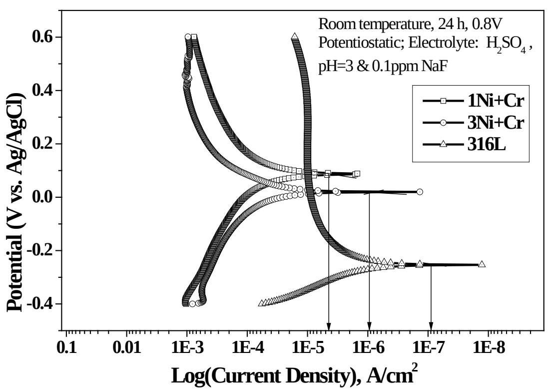

Fig. 10. Corrosion electric potential of red copper substrate with nickel and chromium coating and stainless steel substrate

Results and discussion

The results show that the original electrical conductivity of red copper is about 10^5S/cm. In current study, we choose red copper as a substrate to keep the electrical conductivity in a sufficient level for metallic-FC; which is higher than stainless 304 ($1.68*10^4$ S/cm) and 316L($1.55*10^4$ S/cm). To prevent the corrosion of these red copper substrate, different surface coating layers are deposited on it; such as chromium, zinc and phosphor etc. The electrical conductivity of these copper-based metallic plate are measured in our lab in ordered as follow; red copper stands at C1100H($6.07*10^5$) > chromium-coated red copper($4.01*10^5$) > brass($1.56*10^5$) > phosphor bronze ($9.58*10^4$). In liquid acid environment for FC cathode and anode, experimental results show that the corrosive electric current of copper substrate exceeds 1μA/cm^2, which reach the target of <1μA/cm^2 set by the U.S. Department of Energy (DOE). Therefore, copper substrate must have a corrosion-resistant coating with good conductivity for use in the polarized plate of fuel cell. In the experiment on the corrosive electric current of nickel- and chrome-coated copper substrate, experimental parameters, as shown in Table 1, are single nickel-layer coating thickness at about 40μm, three nickel-layer thickness at 45μm, and single thin chromium-layer coating thickness at 0.25μm, with all the conductivity exceeding 10^5S/cm, proving the coatings' ability to uphold conductivity at a certain level. After subjection to $0.8V_{NHE}$ constant electric current for 24 hours, experiment on corrosive electric current was carried out, with the value of three nickel + chromium layers reaching $9.97*10^{-7}$ A/cm^2 and the value of single nickel + chromium value at $4.36*10^{-6}$ A/cm^2. Despite its ability to meet the DOE standard, it not advisable to adopt the three nickel-layer coating, due to the higher cost resulting from its thickness, less consistency in the flow channel of bipolar plate after stamping, and propensity for cracking after extrusion, causing corrosion. The experiment also showed the densities of the corrosive electric currents of stainless steels 304 and 316L reached $2.88*10^{-9}$ A/cm^2 and $9.81*10^{-9}$ A/cm^2, respectively, both meeting the DOE standard. After subjection to $0.8V_{NHE}$ constant electric current for 24 hours, the density of the corrosive electric current of stainless steel stands at $8.91*10^{-8}$ A/cm^2, still conforming the standard value, making it a suitable material for metal substrate.

4. CONCLUSION

As shown from several completed studies and measurements, stainless steel 316L appears to be a desirable material for the substrate of metal bipolar plate. In addition, after subjection to $0.8V_{NHE}$ constant electric current for 24 hours, the density of its corrosive electric current stands at $8.91*10^{-8}$ A/cm^2, meeting the standard, on top of its good heat conductivity, lower cost for batch production, and corrosion resistance.

In light of the aforementioned data, the materials of bipolar plate, in their choice or modification, must be corrosion-resistant under the operating conditions (with specific electrode potential, oxidant, and reducing agent) of stack, to attain the requirement for fuel cell life cycle. In addition, the materials of bipolar plate must be good heat conductor, so that battery can smoothly dissipate heat, released by fuel and oxidant in their eletrochemical reaction. Moreover, it is advised to select bipolar-plate materials suited to batch production, to cut stack production. Therefore, iron-based alloy, mainly stainless steel, is an advantageous material for fuel-cell bipolar plate and is the development trend.

The study offer help on metal bipolar plate and fuel cell performance. In conclusion, the corrosion properties of metal bipolar plates in PEM fuel cell stack for the future modification or coating characteristics can be improved by experiment and analysis of bipolar plate.

5. REFERENCES

Greenwood, J. A., and Williamson, J. P., 1966, "Contact of Nominally Flat Surfaces," *Proc. R. Soc. London*, Ser. Vol.295, pp.300–319 (1966).

Ihonen, J., Jaouen, F., Lindbergh, G., and Sundholm, G., "A Novel polymer electrolyte fuel cell for laboratory investigations and in-situ contact resistance Measurements," *Electrochim. Acta*, Vol.46, pp.2899–2911 (2001).

Kusoglu, A., Karlsson, A. M., Santare, M. H., Cleghorn, S., and Johnson, W. B., "Mechanical response of fuel cell membranes subjected to a hygro-thermal cycle," *Journal of Power Sources*, Vol.161, pp.987-996 (2006).

Lai, X., Ni, J., Peng, L., Lan, S., and Lin, Z., "Robust design of assembly parameters on membrane electrode assembly pressure distribution," *Journal of Power Sources*, Vol.172, pp.760-767 (2007).

Liu, D. Peng, L. and Lai, X. "Effect of dimensional error of metallic bipolar plate on the GDL pressure distribution in the PEM fuel cell" *Journal of Hydrogen Energy*, Vol.34, pp.990-997 (2009).

Mishra, V., Yang, F., and Pitchumani, R., "Measurement and prediction of electrical contact resistance between gas diffusion layers and bipolar plate for applications to PEM fuel cell," *Journal of Fuel Cell Science and Technology* (2004).

Tawfik, H., Hung, Y., and Mahajan, D., "Metal bipolar plates for PEM fuel cell—A review," *Journal of Power Sources*, Vol. 163, pp.755-767 (2007).

Vlahinos, A., Kelly, K., D'Aleo, J., and Stathopoulos, J., "Effect of material and manufacturing variations on membrane electrode assembly pressure distribution," Proceedings of First *International Conference on Fuel Cell Science, Engineering and Technology* (2003).

Vlahinos, A., Kelly, K., Mease, K., and Stathopoulos, J., "Shape optimization of fuel cell molded-on gaskets for robust sealing," Proceedings of Fourth *International Conference on Fuel Cell Science, Engineering and Technology*, 97106 (2006).

Wang, H., Sweikart, M. A., and Turner, J. A., "Stainless steel as bi-polar plate material for polymer electrolyte membrane fuel cells," *Journal of Power Sources* Vol.155, pp.243-251 (2003).

Zhang, L., Liu, Y., Song, H., Wang, S., Zhou, Y., and Hu, S. J., "Estimation of contact resistance in proton exchange membrane fuel cells," *Journal of Power Sources* Vol.162, pp.1165-1171 (2006).

Zhou, P., Wu, C. W., and Ma, G. J., "Contact resistance prediction and structure optimization of bipolar plates," *Journal of Power Sources* Vol.159, pp.1115-1122 (2006).

燃料電池之金屬雙極板燃料電池腐蝕現象探討分析研究

洪建儒 林昭安 陳韋任 許桓瑞
國立清華大學動力機械工程學系

陳斌豪
國立臺北科技大學車輛工程系

摘要

本研究針對燃料電池之金屬雙極板流道導致腐蝕現象探討，然而金屬雙極板於電化學反應過程中易導致腐蝕現象，導致介面阻抗的增加，亦是整體燃料電池性能之關鍵因素，選擇不易腐蝕又能夠具備低阻抗之金屬便是重要的考量之一，其目的在於有效的與 MEA 接觸以降低接觸阻抗。採用實際金屬流道沖製與電化學實驗量測之分析與量測，即可推論現有電池組性能與結構特性之間的關係並利用不同導電性佳之金屬基材進行其阻抗與模擬質子交換膜(PEM)燃料電池之腐蝕電流特性進行實際量測分析，利用實驗量測與觀察金屬基材的外觀及其阻抗性能，找出金屬於耐腐蝕能力與性能之間的關係。