Digital Light Processing 3-Dimensional Printer to Manufacture Electrolyzer Bipolar Plate

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Abstract. Bipolar plate is one of the largest and most important components in Polymer Electrolyte Membrane Electrolyzer and Fuel Cell that functions as a cell separator, electrical and heat conductor, reactant feed distributor, for the flow of gas-liquid mixture and supporting components for the Membrane Electrode Assembly. In general, injection, compression moulding or Computer Numerical Control-machines are commonly used to produce bipolar plate. These methods, however, cannot be used to produce complex 3-dimensional shapes, such as vertically inverted cone shape or creating a channel inside the plate. By using a 3-dimensional printing machine with laser-based stereolithography or digital light processing, complex design problems and problems in making channels in the plate can be solved easily. In this study, polymer-based bipolar plate was developed using 3-dimensional printing technology which was made conductive by introducing nickel and gold layers through spray coating and electrocoating processes. The nickel layer was optimized by controlling the applied voltage during electrocoating. Since low voltage formed very thin layer whereas high voltage caused “burning” of the sample, applied voltage of 5V was found to be the optimum condition. Employment of gold layer increases the conductivity from 300 S cm$^{-1}$ to 400 S cm$^{-1}$ which enabled the corrosion current density to drop to $0.470 \mu$A cm$^{-2}$, meeting the standard set by US Department of Energy. The porosity test also proved that the bipolar plate was impermeable to hydrogen gas. Therefore, this manufacturing method has great potential to be used for the production of sophisticated electrolyzer cell or fuel cell in the future.

Keywords: polymer bipolar plate, PEMEL, water electrolyzer, digital light processing

1. Introduction
Water electrolysis technology is found promising in generating hydrogen [1], particularly Polymer Electrolyte Membrane Electrolyzer (PEMEL). PEMEL has better performance than the conventional electrolyzer as it could produce hydrogen with higher purity, operate under higher current density resulting in faster gas production, operate at higher pressure and easier to transport as no liquid electrolyte involved [2–4]. However, extensive use of PEMEL as hydrogen generator is retarded by its high cost, where a large portion of this cost is contributed by the bipolar plate (BPP). BPP is one of the
PEMEL components, which has a hollow metal-based plate shape and located between two adjacent cells within the PEMEL. It is responsible for ensuring proper development and operation of PEMEL system, particularly in supporting the stack structure, conducting heat and current between each cell, distributing the feedwater as reacting and cooling agent within the system and also transporting the liquid-gas mixtures [2,4,5]. Since it acts as a multifunctional component, the BPP must possess several features including high mechanical strength and high shock durability, ability to conduct electric and to withstand corrosion as well as commercial viability [2,4]. However, these demands have restricted the material choice for the BPP resulting in the utilization of expensive material and consequently lead to high-priced BPP [3].

The material used for BPP in PEMFC like carbon- and most of metal-based [6] are not suitable to be employed in PEMEL due to high anodic potential in PEMEL [4], where it tends to damage carbon and metal. Titanium (Ti)-based BPP has been widely used because it has most of the indispensable qualities for BPP. Nonetheless, less conductive oxide layer is prone to form on its surface, which increase its ohmic resistance and subsequently reduce the cell performance [2]. Coating the expensive Ti with gold or platinum may solve this issue, but it would further increase the overall cost. Besides, few attempts to fabricate titanium-free BPP for PEMEL have also been made using graphite and stainless steel [7,8]. The highly-conductive graphite however is brittle and chemically unstable. Meanwhile, less expensive stainless steel tends to corrode in acidic environment and the dissolved metal ions would damage the membrane and catalyst, which consequently lower the BPP performance [5]. The need of coating layer for chemically unstable material also lead to an increase in cost [3,5]. After all, the high material and assembly cost for BPP in PEMEL contributes up to around 40% of the entire stack cost [9,10].

Another main concern of BPP is its weight as BPP is the largest contributor to the total weight of PEMEL or even PEMFC system [6,11]. Besides, the widely employed fabrication techniques of BPP such as machining and compression moulding involve complex processing protocols, expensive technology and production of unusable by-products [2,3,12,13]. Hence, the idea of fabricating single piece BPP through 3D printing technology offers attractive solution as it is capable of reducing BPP’s weight, minimizes material consumption and simplifies the assembly of product which consequently decrease the overall cost [13]. In principle, 3D printing is an approach to construct object by depositing materials layer upon layer using a digital computer aided design model [14]. The adoption of 3D printing in manufacturing industries is emerging particularly in healthcare, defense/aerospace and automotive sectors [14], attributed to the various benefits offered in terms of design flexibility, manufacturing throughput time, waste production and quality of product [14,15]. In the field of PEMEL, 3D-printing technology based on selective laser melting (SLM) have been typically chosen to manufacture the BPP [16–18]. For instance, Yang et al. recently developed BPP based on stainless steel using the mentioned technique and attained operation voltage as low as 1.779 V at 2.0 A cm$^{-2}$ [16]. The same group improved their 3D printed BPP by inserting additional gold layer which successfully reduced the operation voltage to 1.71 V at 2.0 A cm$^{-2}$ and attained excellent durability over 100 h [17]. However, the BPP produced from this technique has rough surface and requires to be ground with grinding paper [17]. Another promising technique of 3D printing is digital light processing (DLP), where the liquid photopolymer is solidified under the projection of light source [19,20]. The main advantage of DLP over LS is its shorter fabrication time, which will increase its production rate [19].

Therefore, in order to ease the fabrication process of BPP, DLP-based 3D printing has been adopted to replace the conventional method for the fabrication of lightweight polymer-based BPP. Metal coating has also been introduced as conductive layer on the plate since the originally printed BPP was
prepared from non-conductive photopolymer. The conductive layers were made from a double layer of nickel (Ni) and gold (Au). Metal employment allowed the BPP to be electroplated and to function properly in the PEMEL system. The electrical conductivity, corrosion behaviour and porosity test of the BPP were analysed and compared with the relevant technical standard for the BPP that have been set by the US Department of Energy (DOE).

2. Experimental Method

2.1. Bipolar Plate Printing

The bipolar plate used in the experiment was developed in the laboratory using CAD (Autodesk) and 3D Printer (Duplicator 7 WANHAO). The BPP design was first drawn in circular shape with the diameter and thickness of 30 mm and 3 mm, respectively. For easier handling purpose, two small circles (2.5 mm radius and 1.5 mm thick) were also created at the edge of BPP, so that the alligator clip could hold the small circles without interfering with the main part during electroplating. The BPP drawing is illustrated in Figure 1. It was then printed using 3D Printer through layer by layer deposition method and the 3D ink employed was photopolymer (MAGMA Resin Black), which has a non-conductive property. The ink was originally in the liquid form and then it solidified under the exposure of UV light. After being printed, the BPP was cleaned with isopropyl alcohol and finally left to dry naturally.

![Figure 1. Drawing of bipolar plate.](image)

2.2. Bipolar Plate Coating

As presented in Figure 2, the photopolymer BPP was coated with 3 layers of coating material in the following order; Ni-sprayed, Ni-electrocoated and Au-electrocoated. The initial step involves spraying one side of the clean BPP with Nickel conductive painting (SUPER SHIELD) for two times. Next, it was heated for 30 minutes at 65 °C under a nitrogen flow to improve the electrocoating performance. The BPP was then ready to be electrocoated at room temperature using electroplating tool (Universal Plater). As for the electrocoating process, the BPP and stainless steel were employed as cathode and anode, respectively. Prior to the electrocoating process, surface treatment was required for proper adhesion of the electrocoated material. This treatment requires submerging the BPP in beaker containing Electro-Clean Solution and followed by the Surface Activator Solution for 10 seconds each. Rinsing with distilled water was required after each step. After that, the BPP was immersed in the Ni Plating Solution at the operating voltage of 3V and the conductivity was measured for every 30 s. This was done until the maximum conductivity was obtained. All steps were then repeated for other BPPs at various operating voltage, namely 5V and 7V. Finally, all BPPs were further electrocoated with Au at the operating voltage of 3V. The conductivity of Ni-Au coated BPPs were also evaluated for every 30 s till they reached the maximum conductivity. The BPPs were labelled as Ni$_3$-Au$_3$, Ni$_5$-Au$_3$ and Ni$_7$-Au$_3$. 


2.3. Characterization

The performance of the fabricated bipolar plate was then evaluated by electrical conductivity, corrosion and porosity test. Four-points probe (JANDEL) was used to analyse the conductivity of the BPP. In this technique, four equally spaced electrode probes were connected to the surface of BPP and a direct constant current flowed between the two outer probes, while the voltage was measured between the two inner probes. The potentiodynamic polarization test was conducted to analyse the corrosion behaviour of the BPP with the highest electrical conductivity. The back part of the BPP was first painted with copper (CASWELL) layer to make it conductive, which was necessary in this test. The polarization resistance of 1 cm$^2$ of BPP was then measured in a 0.5M H$_2$SO$_4$ at room temperature and a conventional three-electrode cell system was employed, in which an Ag/AgCl was used as the reference electrode, platinum as the counter electrode and the fabricated BPP as the working electrode. The test was performed using Potentiostat (AUTOLAB) and its measurement was made in the potential range between -2V and 2V at a scanning rate of 1 mV s$^{-1}$. A simple porosity test for the BPP with the best electrical conductivity was also carried out at 15 and 30 bars by observing the formation of hydrogen gas bubble in the water.

3. Results and Discussion

BPP was developed from a non-conductive polymer using 3D printing. Since the BPP will be used to convey electrical current between cells in PEMEL, it must be made conductive. For this purpose, Ni and Au were chosen as metal coating. This is because Ni has excellent electrical conductivity and lower rate of oxidation in comparison to copper, which is also a commonly used conductive material. Meanwhile, less reactive material like Au is required to further reduce risk of oxidation of Ni layer which will deteriorate the overall performance. Besides, Au also possesses high electrical conductivity, which is required for BPP. The initial step involves spraying one side of the clean BPP with Ni conductive painting. The BPP surface was sprayed two times to ensure that the Ni layer was homogenously distributed. Then, attempt has been taken to directly deposit the Au layer onto as-prepared Ni layer through electrocoating, but the Au particles were poorly attached on the Ni-layer. The reason lies in the fact that the conductivity of Ni-spray layer was low (around 30 $\Omega$), such that it could not provide good adhesion for Au electrocoating. Therefore, another Ni layer was electrocoated prior to Au since similar material has better adhesion. The presence of this layer increases the conductivity and subsequently improves the adhesion property of Au.

The DOE has formulated the target for BPP in PEM fuel cell (PEMFC) [21], where certain targets are also applicable to the BPP in PEMEL. One of the targets is that the electrical conductivity of BPP must be at least 100 S cm$^{-1}$. Therefore, the conductivity of the fabricated sample in this work were tested for comparison purpose. Four-points probe was used to study the conductivity of the BPP and the measurement was
Figure 3. Conductivity-time curves of BPP after coating with (a) Ni$_3$-Au$_3$, (b) Ni$_5$-Au$_3$ and (c) Ni$_7$-Au$_3$, where (i) represents after Ni coating and (ii) represents after Ni-Au coating, taken for every 30s until the maximum conductivity was obtained. In order to ensure the reliability of the results, several samples were prepared, and their average conductivity was taken. The electrical conductivity was then calculated using the following equation (eq. 1):

$$\sigma = \frac{I}{2\pi s V}$$

where $\sigma$ is the conductivity (S cm$^{-1}$), $V$ is the voltage (V), $I$ is the current (A) and $s$ is the probe spacing (cm). The corresponding conductivity-time curves were then plotted as in Figure 3 (a)-(c). The corresponding (i) and (ii) diagrams illustrate the conductivity-time curves for the BPP after electrocoated with Ni and the overall conductivity-time curves for the BPP after electrocoated with Ni-Au, respectively.

As shown in Figure 3, all bipolar plates with various electroplating voltage were conductive indicating that this manufacturing technique was successful in fabricating the BPP. Figure 3 (a)-(c) i clearly show that as the voltage increases, the maximum conductivity was obtained in shorter period. The best conductivity was shown by the BPP electrocoated with Ni at 5V, which achieved 300 S cm$^{-1}$ in 1000s. After the maximum conductivity for Ni layer was acquired, Au was electrocoated onto the BPP and the overall conductivity of every sample shows improvement. The conductivity still follows similar trend even after Au coating where Ni$_5$-Au$_3$ sample has the best electrical conductivity followed by Ni$_7$-Au$_3$ and Ni$_3$-Au$_3$. Hence, it indicates that the final conductivity strongly depends on Ni coating. The highest conductivity recorded in this study was near 400 S cm$^{-1}$ for Ni$_5$-Au$_3$, which is four times greater than DOE requirement for a standard BPP. Since the deposition current density affects the thickness of coating layer [22], it is postulated that the thickness of coating layer is also influenced by the voltage applied during electrocoating process. This idea could be explained using the correlation between current density and applied voltage. As shown in eq. 2, current density ($J$) is by definition the current ($I$) per unit area (A), while the Ohm’s Law (eq. 3) states that the amount of electrical current (I) flow in a circuit is directly proportional to the voltage (V) at constant resistance (R).
By combining eq. 2 and eq. 3, the following equation is derived:

\[ V = JAR \]

Therefore, assuming that the area and resistance are constant, the applied voltage is proportional to the current density. Hence, it could be concluded that lower electrocoating voltage results in thinner coating layer and vice versa. This may explain why the BPP coated with \( \text{Ni}_3\text{Au}_3 \) has the lowest conductivity, which was around 80 S cm\(^{-1}\). Nonetheless, the \( \text{Ni}_7\text{Au}_3 \) sample did not simply obey this trend. Besides having lower conductivity than the BPP coated with \( \text{Ni}_5\text{Au}_3 \), its surface was also darker in comparison to other samples. The appearance of the darker BPP, which is also known as “burning” was attributed to the high operating voltage during electrocoating. At the operating voltage of 7V, the inadequate mass transfer depleted the electrolyte around the cathode and subsequently caused the undesired reactions like the deposition of metal hydroxide, which then resulted in the surface “burning” [23]. Meanwhile, the low conductivity of the \( \text{Ni}_7\text{Au}_3 \) sample might be ascribed to the formation of pinholes and cracks on Ni layer, which were created during the removal of residual stress. This internal stress was previously developed by coincidence when the high operating voltage was applied during electrocoating process [22].

High corrosion resistance, which is also interpreted as high stability, is one of the most important requirements for BPP since the operating environment in PEMEL is very harsh. In this regard, the DOE has also set the maximum corrosion current density for the BPP to be at 1 \( \mu \text{A/cm}^2 \) [21]. In this analysis, the corrosion behaviour of the BPP with highest electrical conductivity (\( \text{Ni}_3\text{Au}_3 \)) was investigated in potentiodynamic polarization test. A conventional three-electrode cell system was employed and the polarization resistance of 1 cm\(^2\) of BPP was then evaluated in a 0.5M \( \text{H}_2\text{SO}_4 \) at room temperature. Using Potentiostat, the measurement was made at a scanning rate of 1 mV s\(^{-1}\) in the potential range between -2V and 2V. Figure 4 presents the potentiodynamic polarization behaviour of the BPP coated with \( \text{Ni}_3\text{Au}_3 \). The rate of corrosion was then calculated using the following equation (eq. 5):

\[ CR = \frac{tM_{\text{corr}}}{nFp} \]

where CR is the corrosion rate, \( t \) is the exposure time, \( I_{\text{corr}} \) is the corrosion current density, \( M \) is the molar mass of gold, \( n \) is the number of electrons involved in the corrosion reaction, \( F \) is the Faraday’s constant and \( p \) is the standard density. From the intercept of the Tafel slope, the corrosion current density (\( I_{\text{corr}} \)) and corrosion potential (\( E_{\text{corr}} \)) were approximately 469.700 mA cm\(^{-2}\) and 548.160 mV, respectively and hence, the calculated corrosion rate is 2.0015E\(^{-5}\) per year. Additionally, the \( I_{\text{corr}} \) value also meets the DOE standard for BPP, where it must be less than 1 \( \mu \text{A/cm}^2 \) [21].
The porosity test was also conducted on the BPP Ni₅-Au₃. Hydrogen was applied to the BPP for five minutes at 15 and 30 bars. After 5 minutes, the formation of bubble was not observed in the water even at the elevated pressure and thus, this implies that the BPP is impermeable to gas.

4. Conclusion
Digital light processing based-3D printing was successfully demonstrated to fabricate the photopolymer bipolar plate. As it must be made conductive, the bipolar plate was first sprayed with nickel and then electrocoated with nickel and gold. The ability of the bipolar plate to be electrocoated with nickel and gold layer proves that the nickel-spray is suitable to be employed for preparing the surface for electroplating operation. The results showed that the bipolar plate that has the best electrical conductivity was the one that was electrocoated with nickel and gold at the operation voltage of 5V and 3V. Its conductivity was measured roughly around 400 S cm⁻¹, whereas its corrosion current density was 0.470 µA cm⁻². Therefore, both conductivity and corrosion tests presented that the sample meets the Department of Energy standard for bipolar plate. In addition to that, the porosity test verified that the bipolar plate was impermeable to gas. This concludes that this manufacturing process is promising for the bipolar plate. Extensive exploration of this method for other components in Polymer Electrolyte Membrane Electrolyzer and Polymer Electrolyte Membrane Fuel Cell is recommended to further reduce the bipolar plate cost. This facile technique produced lightweight and price-competitive bipolar plate with desirable properties like good electrical conductivity, good corrosion resistance and impermeable to gas.

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References
[1] Stamenkovic V R, Strmcnik D, Lopes P P and Markovic N M 2016 Nat. Mater. 16 57–69
[2] Chisholm G, Kitson P J, Kirkaldy N D, Bloor L G and Cronin L 2014 Energy Environ. Sci. 7 3026–32
[3] Gago A S, Ansar A S, Gazdzicki P, Wagner N, Arnold J and Friedrich K A 2014 ECS Trans. 64 1039–48
[4] Lædre S, Kongstein O E, Oedegaard A, Karoliussen H and Seland F 2017 Int. J. Hydrogen Energy 42 2713–23
[5] Langemann M, Fritz D L, Müller M and Stolten D 2015 Int. J. Hydrogen Energy 40 11385–91
[6] Karimi S, Fraser N, Roberts B and Foulkes F R 2012 Adv. Mater. Sci. Eng. 2012
[7] Jung H Y, Huang S Y, Ganesan P and Popov B N 2009 J. Power Sources 194 972–5
[8] Nikiforov A V., Petrushina I M, Christensen E, Tomás-García A L and Bjerrum N J 2011 Int. J. Hydrogen Energy 36 111–9
[9] Ayers K E, Capuano C and Anderson E B 2012 ECS Trans. 41 15–22
[10] Carmo M, Fritz D L, Mergel J and Stolten D 2013 Int. J. Hydrogen Energy 38 4901–34
[11] Rafiuddin, Arshad M, Saleem A, Shahzad M, Subhani T and Hussain S 2016 J. Thermoplas. Compos. Mater. 29 1315–31
[12] Bourell D L, Leu M C, Chakravarthy K, Guo N and Alayavalli K 2011 CIRP Ann. 60 275–8
[13] Gould B D, Rodgers J A, Schuette M, Bethune K, Louis S, Rocheleau R and Swider-Lyons K 2015 ECS J. Solid State Sci. Technol. 4 P3063–8
[14] Schniederjans D G 2017 Int. J. Prod. Econ. 183 287–98
[15] Ngo T D, Kashani A, Imbalzano G, Nguyen K T Q and Hui D 2018 Compos. Part B Eng. 143 172–96
[16] Yang G, Mo J, Kang Z, List F A, Green J B, Babu S S and Zhang F Y 2017 Int. J. Hydrogen Energy 42 14734–40
[17] Yang G, Yu S, Mo J, Kang Z, Dohrmann Y, List F A, Green J B, Babu S S and Zhang F-Y 2018 J. Power Sources 396 590–8
[18] Jayakumar A 2018 MATEC Web of Conferences 172 4005
[19] Wang X, Jiang M, Zhou Z, Gou J and Hui D 2017 Compos. Part B Eng. 110 442–58
[20] Patel D K, Sakhaei A H, Layani M, Zhang B, Ge Q and Magdassi S 2017 Adv. Mater. 29 1–7
[21] U.S. D of E 2012
[22] Wang H C, Hou K H, Lu C E and Ger M Der 2014 Thin Solid Films 570 209–14
[23] Jensen J A D, Pociwiarowski P, Persson P O., Hultman L and Møller P 2003 Chem. Phys. Lett. 368 732–7