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Electroforming of metallic bipolar plates with micro-featured flow field

Shuo-Jen Lee*, Yu-Pang Chen, Ching-Han Huang

Department of Mechanical Engineering, Yuan Ze University, 135 FarEast Road, NeiLi, TaoYuan, Taiwan, ROC

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Abstract

In addition to mechanical properties, uniform fuel dispersion, efficient removal of water and high electric conductivity are also important functions of a bipolar plate. The capillary effect of micro-featured flow field may attract water from the carbonic diffusion layer and promote more evenly dispersion of fuels into the diffusion layer. Thus, it may improve the performance of proton exchange membrane (PEM) fuel cells.

In this research, the Lithography Galvanik Abformung (LIGA) manufacturing processes with electroforming technology are investigated for the production of micro-featured flow field of the metallic bipolar plates. The micro-features are designed in conjunction with the existing flow channel to form an integrated flow field system. Instead of silicon wafer, a 4 in. wafer size SS304 stainless steel plate is used as the substrate. The LIGA processes of photo masking, spin coating, exposure and development are employed to create electric conducting die with flow field pattern. Electroforming of this metallic plate coated with flow field patterned photo resist will result in the main flow channel on the SS304 plate. The same processes were conducted for the second iteration to form micro-features. Thus, metallic bipolar plates with micro-features are produced using the electroforming technology.

A single cell with total cell area of 16 cm^2 and reaction area of 4 cm^2 was produced. It has micro-features of 100 and 200 μm width and of 50 μm depth. The dimensions of the main flow channel were 300 μm in width and 200 μm in depth. Single cell tests were conducted to evaluate its performance. The cell performance of the single cell with SS304 metallic bipolar plates exceeds similar size single cell with silicon or glass fiber substrates. The electroforming is a promising technology for metallic bipolar plates with micro-features and micro-fuel cell.

Keywords: LIGA; Electroforming; Micro-features; PEM fuel cell; Flow field pattern

1. Introduction

The pursuit for high efficient and low pollution green energy source has accelerated the R&D in fuel cells. The potential in proton exchange membrane (PEM) fuel cells for its applications and market has also attracted great attention [1]. The fuel cells also inherit the beneficial features of modularity, light weight and small volume size [2]. Especially in the 3C industries, the power density of a fuel cell may exceed three times of the lithium battery and has the advantage of re-fuelling [3].

The fuel cells for 3C applications require thinner bipolar plates with good conductivity and fuel flow. Lee et al. [4] created flow channels with depth between 50 and 200 μm on the silicon wafer. By using sputtering and other MEMS processes, it became bipolar plates. The micro-fuel cell performed normally with cell efficiency of 50 mA cm^{-2}. However, the silicon-based bipolar plate had conductivity of only 0.5 S cm^{-1} which was 10,000-fold smaller than 5000 S cm^{-1} of a metallic bipolar plate. Yu et al. [5] had developed dry etching process, RIE, on silicon wafer for 200 μm depth of flow channel. Metal sputtering of 0.5–1.5 μm Au, Cu or Ti created the surface conducting film. The results indicated that micro-featured flow field of the silicon-based bipolar plates would provide more uniform distribution of fuels over graphite bipolar plates under the same operating conditions

* Corresponding author. Tel.: +886 3 4638800; fax: +886 3 4558013.
E-mail address: mesjl@saturn.yzu.edu.tw (S.-J. Lee).

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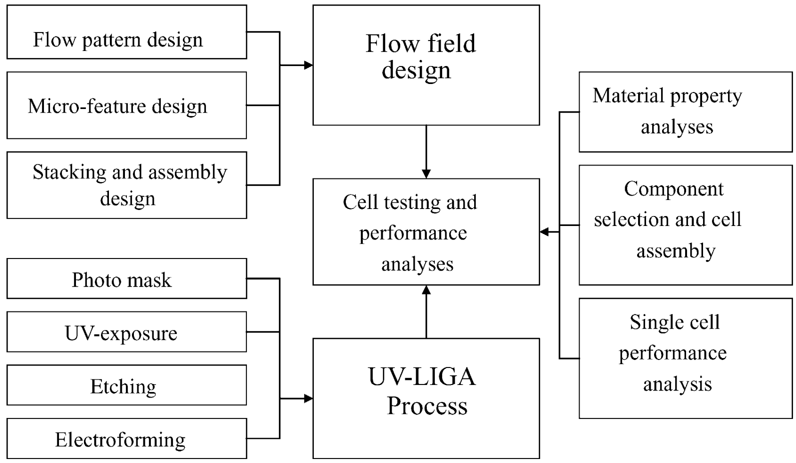

Fig. 1. Flow chart of research methodology.

of gas pressure and flow rate. However, high resistance still restrained its performance improvement. The cell packaging of the silicon-based MEMS process may further increase total contact resistance and, thus, limit the performance of silicon-based PEM fuel cells.

In 2003, Mench et al. [6] had successfully developed a direct methanol (DM) fuel cell of 1 W power in 1 cm^3. The capillary effect was employed to promote self-induced fluid flow. It proved that by better understanding of micro-physical phenomena would produce compact, efficient and modular fuel cell design. Schmitz et al. [7] applied PCB process in the manufacturing of bipolar plates. A 1500 h of cell life test was conducted which proved the feasibility of portable fuel cells. But, it current density was not as good as expected. It may be caused by the shallow (35 μm) copper flow channel and poor conductivity of glass fiber substrate. The shallow flow channel creates large resistance to fuel flow. The poor conductivity results in significant internal resistance. O'Hayre et al. [8] succeed in designing a 16-cell PEM fuel cell in a 3.5 $in.^2$ glass fiber composite plate. It achieved open circuit voltage of 12 V for a 3C battery. However, the cell performance still suffered from the huge contact resistance. In addition, the glass fiber substrate does not have enough mechanical strength to sustain the stacking pressure of a stacking design. Therefore, planar type of cell design was tested.

The metallic bipolar plates would provide high mechanical strength and electric conductivity. However, it is inefficient or non-practical to produce micro-featured flow pattern. The electroforming is a nano-scale metallic deposition process, which can create precise and detailed forms. It is one of the feasible technologies to create flow field and micro-features on metallic bipolar plates. Hemker and Last [9] reported the Young's modulus from the electroforming of Ni was 180 ± 24 GPa which is much higher than cast Ni. It also had higher hardness. Hirata [10] reported that electroforming had high precision (±0.5 μm), high aspect ratio (depth/width ratio exceeds 10) and thick forming layer (exceeds 200 μm). Maleka and Saile [11] demonstrated injection-molding die with micro-features by the electroforming technology.

2. Design and production of metallic bipolar plates with micro-features

The size of the bipolar plates should be smaller than 4 in. diameter which is the standard size for MEMS processes. The dimension and tolerances of flow field pattern and micro-features should conform to the capability of the MEMS processes. The thin thickness of the cell may require careful considerations in stacking and assembly design. Selected processes of the Lithography Galvanik Abformung (LIGA) technology such as photo masking, UV-exposure, etching and electroforming were employed for this research to form flow field with micro-features. A single cell is assembled for cell performance test. The flow chart of research methodology is presented in Fig. 1.

2.1. *Design of metallic bipolar plates*

A 4 in. diameter SS304 stainless steel thin disk with 0.6 mm in thickness is used as the substrate. Its shape and size is similar to a 4 in. wafer. Two bipolar plates for a single cell assembly were design in a single disk. Therefore, the oversize of the bipolar plate is 4.0 cm × 4.0 cm. The width of the main flow channel, referred from the results of [4,8], was selected to be between 200 and 300 μm. The thickness of photo resist from the spin coater in our research is also about 250 μm. The depth of the channel was 200 μm taking pressure drop and flow resistance into consideration. Micro-features are designed with width of 100 and 200 μm and depth of 50 μm. Because the metallic plate is strong, the flow field plates combined the functions of flow field channel, the current collector and end plate. A 6 mm diameter fuel connector was glued on both fuel inlet and outlet. The single cell design with all of the cell components is shown in Fig. 2.

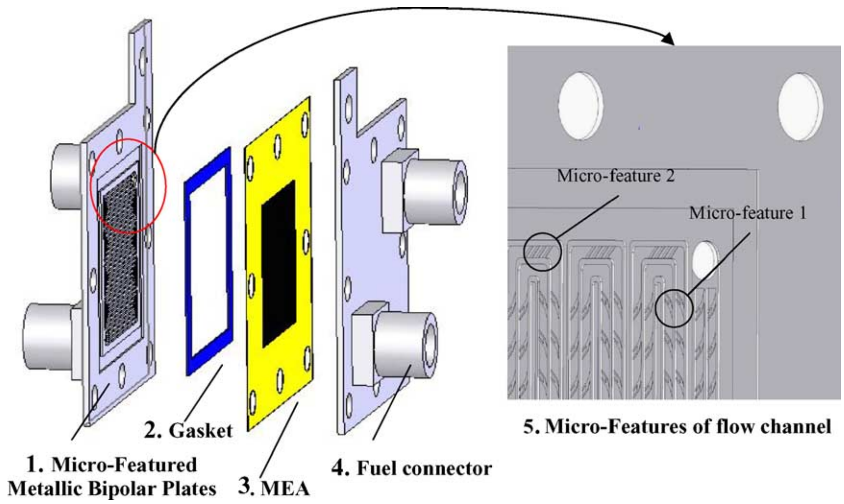

Fig. 2. Single cell design and its components.

The main flow field pattern is of serpentine structure. The micro-features are in 45° angles to the flow direction. The opening is wider in the inlet side of the micro-channel than in the outlet side. It is hope that fuel may flow more easily into the "land" region and thus improves fuel distribution. The layout of the flow field plate on the 4 in. stainless disk is presented in Fig. 3. Photo mask of the flow field plate design is shown in Fig. 4.

2.2. Pattern creation processes—spin coating, exposure and development

The developed, baked and harden photo resist will form flow pattern for electroforming. Therefore, the selection of photo resist may greatly affect the quality of electroforming. The conventional photo resist for MEMS process is thin. The thickness of photo resist after spin coating is around 10–50 μm. It is too thin for the main flow field pattern. After many trials, the SU-8 photo resist is found to meet our research goal of obtaining a 250–300 μm thickness of photo resist after spin coating.

The SS304 stainless disk is first degreased and cleaned with ultrasonic de-ionized water. It is pre-treated with special chemical to improve adhesion between the substrate and the electroformed metal. After another cleaning operation, the SS304 stainless disk was spin coated with SU-8. It is then soft baked to remove water content in the photo resist. The shape of photo resist is flat and stable and is ready for UV-exposure with the photo mask. The wavelength of the UV light is 365 nm. The exposure time is 50 s. After UV-exposure, cross-link of polymer of the exposed area will resist being etched away by following processes. The disk went through post expose bake (PEB) to enforce the chemical bonding of the cross-linked polymer. Finally, the un-exposed area is etched away leaving photo resist with flow field pattern. The procedures to create the flow field pattern are presented in Fig. 5.

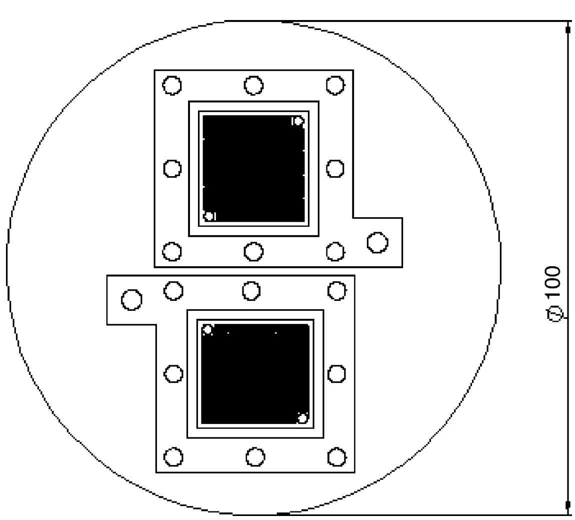

Fig. 3. Design layout of the electroforming cathode plate.

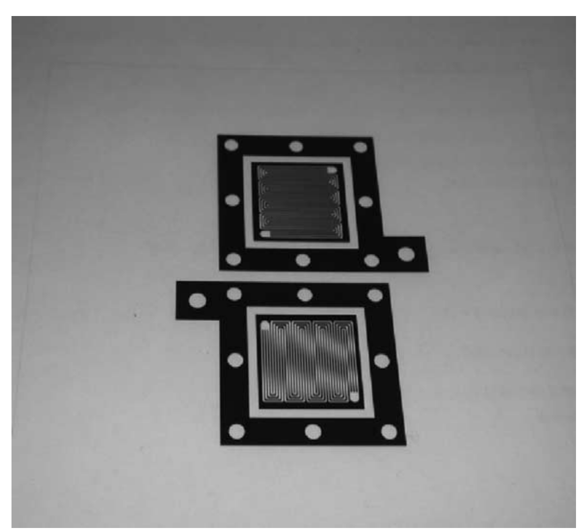

Fig. 4. Photo mask.

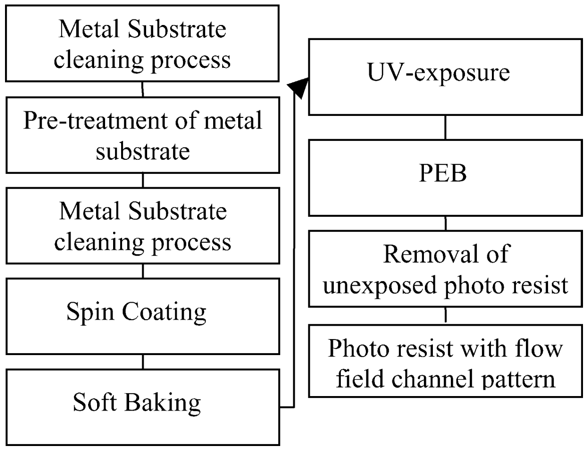

Fig. 5. Procedures of creating flow field pattern.

2.3. *Flow field and micro-features creation processes–electroforming*

Electroforming of Ni is chosen because the technology is mature. The electrolyte is nickel sulfamate. In general, complex geometry of the specimen presents no difficulty. The leveling and uniformity of the plated film are of good quality. The internal stress of the film is low.

The compositions of the electrolyte and the maintenance of the electrolyte are important to the electroforming process. The variables may include conductivity, pH value and additives of the electrolyte. Operating parameters of the electroforming process are also vital to the quality of the final products. They are operating temperature, current density, processing time, fixture design of the cathode and electrolyte agitation. Larger current density may result in coarse metallurgical structure. The thickness of the plated film is proportional to processing time. Higher operating temperature will have better conductivity but may result in de-coloring effect. The procedures of electroforming process are shown in Fig. 6.

Fig. 7 presents the whole process of electroforming of flow field pattern. Fig. 8 shows the electroforming system. It consists of an electrolyte tank, a filtration system and a power supply and control unit. After the electroforming of the first layer of main flow field pattern, the same procedures repeated with the photo mask of micro-features to grow second layer of micro-features on the first layer of main flow field pattern.

3. Results and discussions

3.1. *The spin coating process*

Because the SU-8 is a sticky photo resist and the height of the main flow channel requires to be about 250 μm, the uniformity of the thickness of the photo resist depends a lot on the spinning parameters as well as the spinning speed and the condition of the spin coater. Non-uniformity of photo resist will create problems in following process. First, after PEB, the photo resist may deform especially around the edge. Secondly, if the photo resist of un-exposed area is not etched properly and/or the residue is not properly cleaned, the flow field pattern will have defects. Fig. 9(a and b) show the photo resist of micro-feature 1 and micro-feature 2. They both have some chemical residues on the flow channel. Thirdly, in development stage, it may create over- or under-exposure. Fig. 10 shows the detachment of the photo resist of the over-

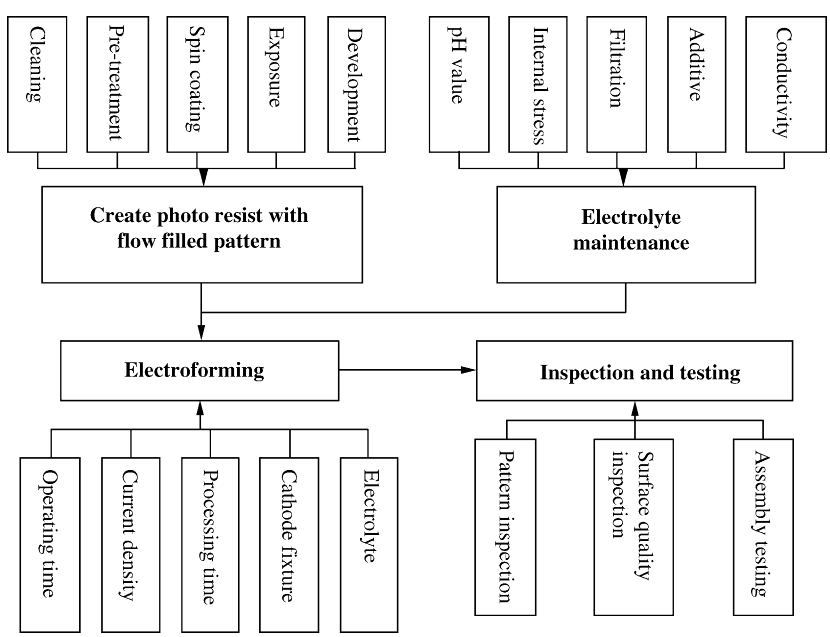

Fig. 6. Procedures of electroforming process.

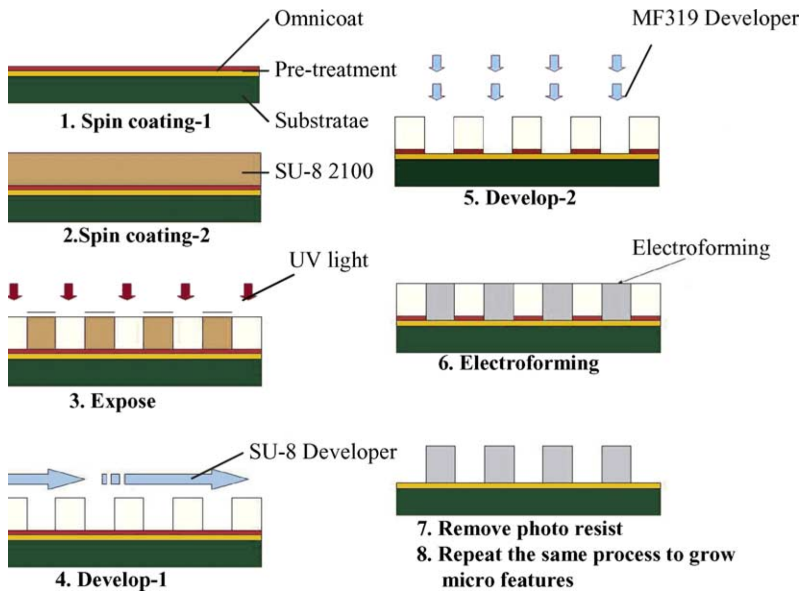

Fig. 7. Flow chart of the whole electroforming process.

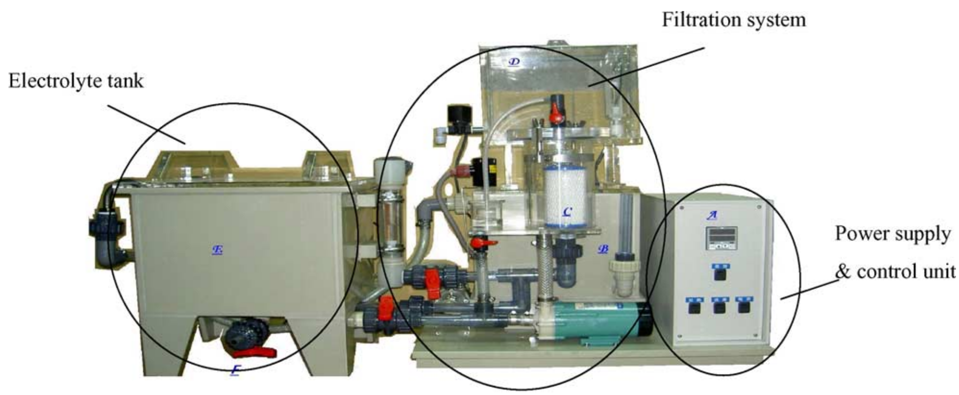

Fig. 8. The electroforming system.

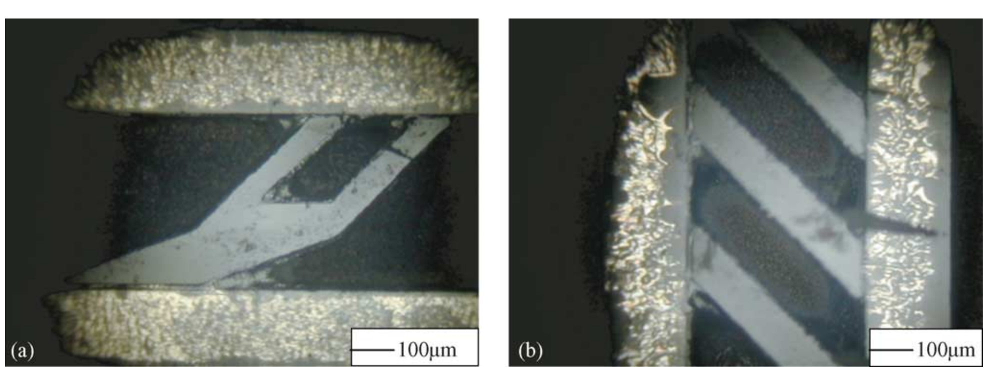

Fig. 9. (a) Photo resist of micro-feature 1 (100 and 200 μm wide) and (b) 2 (100 μm wide).

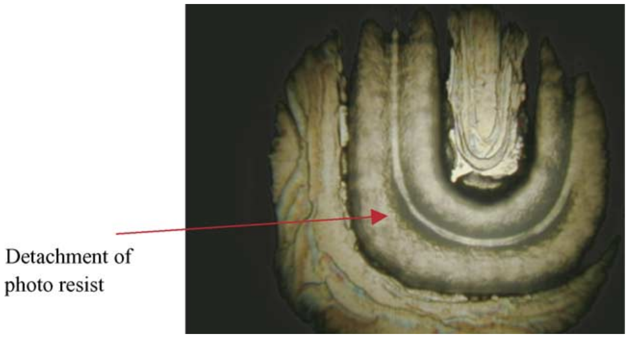

Fig. 10. Picture of over-exposed photo resist.

exposed area. The height of photo resist from this research is between 210 and 310 μm.

3.2. The electroforming process

In order to create the flow field with micro-features, two iterations of the whole electroforming process are conducted. The first iteration of electroforming is to create the main flow field pattern. The second iteration of electroforming is to create the micro-features on the first layer. Fig. 11 shows the first layer electroforming of main flow channels. Fig. 12 shows the second layer electroforming of micro-features.

The optical microscopy, micrometer and laser displacement profiler were employed to exam the surface profile and height of the flow channel. Figs. 13 and 14 present the flow field channel with micro-features. They both demonstrate the integrity of the metallurgical structure of the electroformed flow field pattern. The shape is not very sharp which is caused by the chemical residues left on the pattern before electroforming. There is around 20 μm difference in height over the whole bipolar plates. This might be caused by the initial flatness error of the SS304 disk. It could also be resulted from the non-uniformity of the photo resist.

Fig. 11. First layer electroforming of main flow field channel.

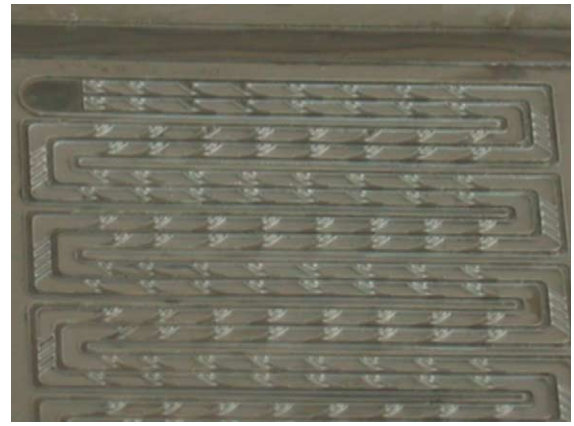

Fig. 12. Second layer electroforming of micro-features.

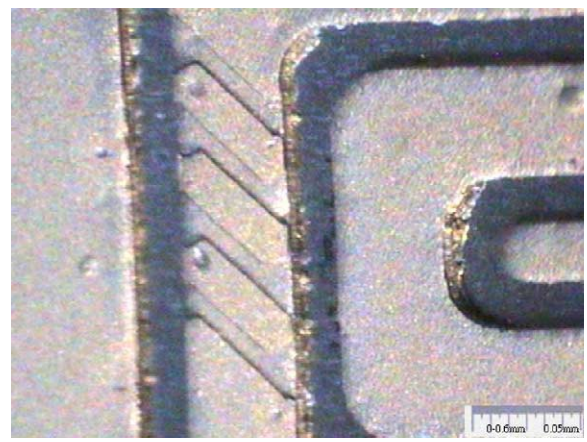

Fig. 13. Photo of electroforming metallurgical structure (main flow channel and micro-feature 2).

3.3. Single cell performance test

A single cell was assembled for cell performance test. The single cell has an overall size of 4 cm × 4 cm with 2.6 mm in thickness. A 5-layered MEA, #597010, from Fuel Cell Store is used which is composed of Nafion 112, GDL of

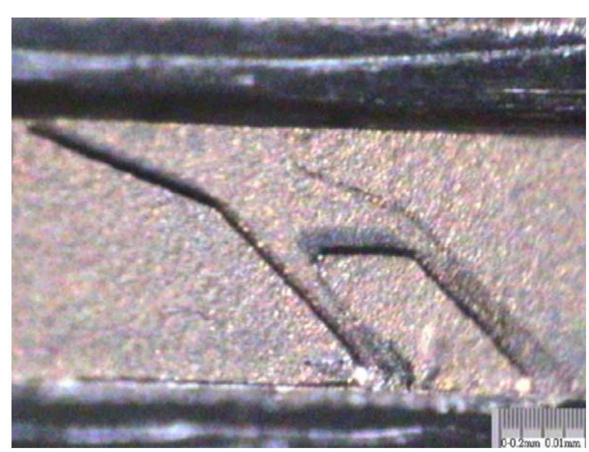

Fig. 14. Photo of electroforming metallurgical structure (micro-feature 1).

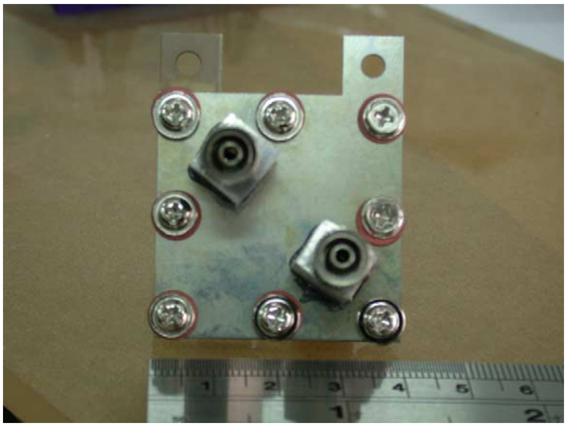

Fig. 15. Prototype of the single cell assembly cell.

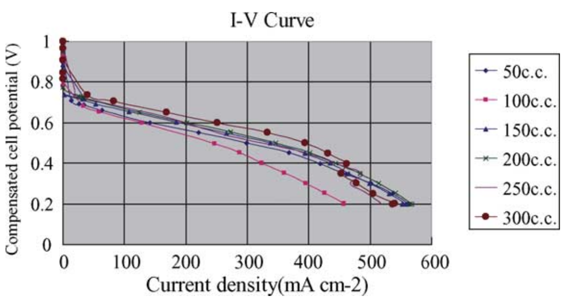

Fig. 16. *I–V* curve of the cell performance tests.

carbon cloth material and 0.5 mg of Pt loading on both anode and cathode. The effective reaction area is 2 cm × 2 cm. The weight of the single cell without the fuel connectors is 24 g. The single cell is shown in Fig. 15.

Cell performance tests are conducted with 50, 100, 150, 200, 250 and 300 standard cubic centimeter per minute (SCCM), respectively. Pure dry oxygen and hydrogen and the cell temperature is controlled at 70 μm. *I–V* curves of these cell performance tests are plotted in Fig. 16. At the initial test of 50 SCCM, the internal flooding is not obvious. The cell performance decreases toward the flow rate of 100 SCCM. The cell performance stabilized when the flow rate exceeds 150 SCCM. For flow rates of 150 and 300 SCCM, the current densities at 0.6 V are 190 and 250 mA cm^{-2}, respectively.

The leveling of cell performance could be caused by blockage of micro-features by the GDL. The thickness of the GDL (0.42 mm) is much larger than that of the micro-features (0.05 mm). The optimal current density is 250 mA cm^{-2} at 0.6 V for flow rate of 300 SCCM. The total current output is 1 A and power output is 0.78 W. The average power density is 195 mW cm^{-2}.

4. Conclusions

The LIGA with electroforming process is employed to grow main flow field pattern with micro-features on SS304 stainless steel plate. The high mechanical strength and good electric conductivity of the metallic bipolar plates make the volume of a single cell small. The reaction area of the prototype of the single cell is 4 cm^2. The overall size is 16 cm^2 with thickness of 2.6 mm. The average power density is 195 mW cm^{-2}. The cell performance is better than similar size of PEM fuel cell on silicon and glass fiber substrates. Better selection of component material and control of component specifications are important in improving cell performance. For example, the thickness of the GDL may have to be reduced. The proposed manufacturing procedures prove to be a promising technology in producing metallic bipolar plates with micro-features.

Acknowledgements

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