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Development of electrically conductive DLC coated stainless steel separators for polymer electrolyte membrane fuel cell

Yasuo Suzuki, Masanori Watanabe, Tadao Toda, Toshiaki Fujii

Plasma Ion Assist Co., Ltd Nakagawara 34-1, Kamitoba, Minami-ku, Kyoto-city, Kyoto, 601-8142 JAPAN

E-mail:y.suzuki@plasma-ion.co.jp

Abstract. Polymer electrolyte fuel cell (PEFC) as one of generation devices of electrical power is rapidly expanding the market as clean energy instead of petroleum and atomic energy. Residential fuel cell goes into quantity production and introduction of fuel cell for use in automobiles starts in the year 2015 in Japan. Critical subject for making fuel cell expand is how to reduce cost of fuel cell. In this paper we describe about separator plate which domains large ratio of cost in fuel cell stack. In present time, carbon is used in material of residential fuel cell separator. Metal separators are developed in fuel cell for use in automobiles because of need of mechanical strength at first. In order to make fuel cell expand in market, further cost reduction is required. But the metal separator has problem that by using metal separator contact resistance occurred by metal corrosion increases and catalyst layer and membrane degrade. In recent time we found out to protect from corrosion and dissolution of metals by coating the film of porous free conductive DLC with plasma ion implantation and deposition technology that we have developed. Film of electrically conductive DLC was formed with high speed of 13μm/hr by ICP plasma, and coating cost breakout was performed.

1. Introduction

Residential fuel cell goes into quantity production in the year 2015 and fuel cell for use in automobiles starts to be produced in the year 2015 and they are mass-produced in the year 2020 in Japan. Ratio of separator cost in stack of fuel cell is 10~20% and reduction of separator cost is important in the spread of fuel cell. In present time carbon separators are used but their cost reduction is difficult. Stainless steel is expected in stead of carbon separator from a viewpoint of cost. It is required that separator cost of residential fuel cell is 150yen in the year 2015 and separator cost of fuel cell for use in automobiles is 50yen in A4 size in the year 2020. The electrically conductive DLC coated stainless steel separator by method of developed plasma ion based ion implantation and deposition is superior to contact resistance and corrosion resistance, and it became possible that separator cost was remarkably reduced by high speed deposition equipment.

2. Characteristics required to separators

2.1. Construction of separator

Fuel cell is constructed from anode electrode, electrolyte membrane, cathode electrode and separators which hold these from both sides. Fuel cell is constructed from single cell which is assembled in series. Anode electrode is constructed from gas diffusion layer (GDL) which consists of carbon paper for diffusing H_2 gas/Air, and catalyst layer.

2.2. Characteristics required to separators

Characteristics required to separators is electrically conductive, little in contact resistance between separator and GDL which is anode electrode or cathode electrode and superior to corrosion resistance of H_2SO_4 solution which occurs by reacting with electrolyte membrane and water. And it is superior to cost performance to be specially required to fuel cell for use in automobiles.

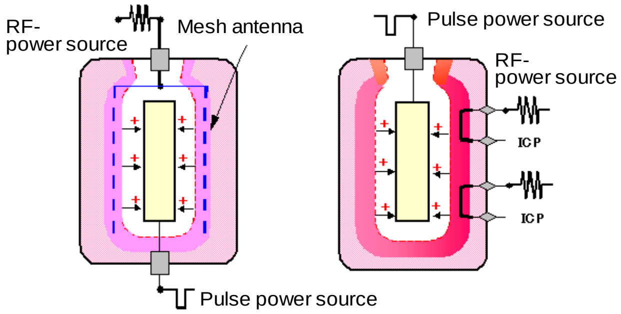
3. Conductivities of DLC

3.1. What is DLC

DLC is Diamond Like Carbon. It is a-C:H which consists of diamond structure sp^3 and graphite structure sp^2. DLC has insulation properties similar to diamond, high hardness and corrosion resistance.

3.2. Method of DLC film formation

Generally DLC film is formed by method of arc-ion plating and sputtering. Formed film is porous because DLC film is formed by sputtering and arc-evaporating solid carbon target. Therefore it can not be avoided to be inferior to corrosion resistance. In method of developed PBIID [1,2,3,4,5] technology (Plasma Based Ion Implantation and Deposition), methane and acetylene gas are ionized by simultaneously applying RF and high pulsed voltage, carbon ion is implanted and deposited to substrate, and electrically conductive DLC film is formed. This film is porous free and superior to corrosion resistance. PBIID has two method, CCP (Capacitively Coupled Plasma) and ICP (Inductively Coupled Plasma). Figure1 shows comparison of two methods. Feature of ICP method is that plasma density is very high and deposition rate is very fast.



No.	1	2
Plasma	Antenna method(CCP)	ICP method
RF-Power source structure	Flat plate /Cylindrical mesh	One turn Coil
Plasma density	~3×10^{10} cm^{-3}	~2×10^{11} cm^{-3}
Plasma uniformity	±20%	±20%
Deposition speed	1μm/hr	5μm/hr (※)

※The distance between substrate and ICP source is 150mm.

Figure 1. DLC film formation by the PBIID method.

3.3. Method to change from insulation properties to electric conduction

DLC has insulation properties essentially to have diamond construction sp^3. When DLC film is formed under 350℃ and B-ion or N-ion is simultaneously implanted to DLC film, insulating DLC film changes to electrically conductive DLC(a-C:H:B, a-C:H:N) film. Electrically conductive DLC film is nano size (10～80nm) crystallized film to grow with pillar-shaped column. Conductivity of DLC film is less than 5mΩ・cm.

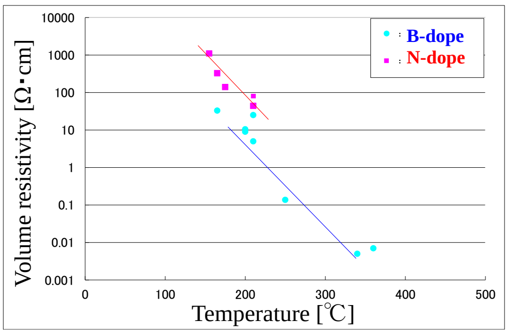


Figure 2. Volume resistivity.

4. Reduction of contact resistance

4.1. Contact resistance (CR) and measurement method

Figure 3 shows measurement method of contact resistance. CR_{sample} is contact resistance between DLC coated sample and GDL. R_{total} is total resistance on measurement. $R_{baseline}$ is resistance except sample.

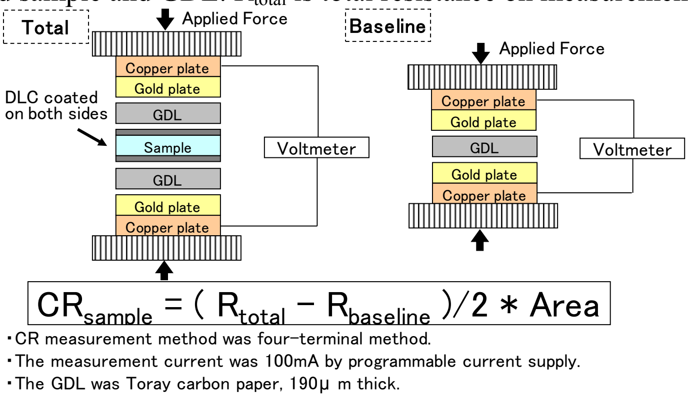


Figure 3. CR Measurement method for coated plates.

4.2. Contact resistance

Electrically conductive DLC film has many contact points which consist of nano size (10～80nm) crystallization to grow with pillar-shaped column. In that result it was able to lower contact resistance by strongly contacting between GDL and electrically conductive DLC film. Figure 4 shows contact resistance on compaction force. It is less than 5mΩ・cm^2.

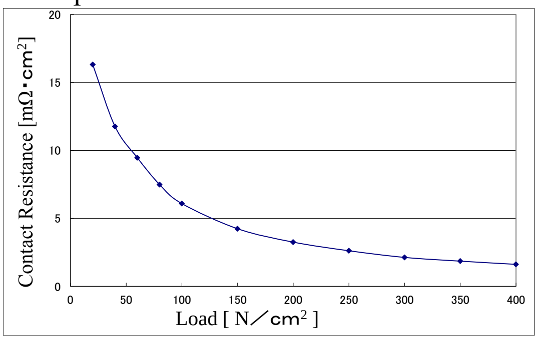


Figure 4. Interfacial resistance dependency on compaction force.

5. Corrosion resistance

5.1. Electrical conductive DLC formation

As shown in Figure6, electrically conductive bi-layer DLC has conductive properties which consists of two kind of DLC film. Top layer DLC film specializes conductive properties. Bottom layer DLC film specializes corrosion resistance. Electrically conductive DLC film is formed at 350℃～. Corrosion resistance DLC film is formed at ～200℃.

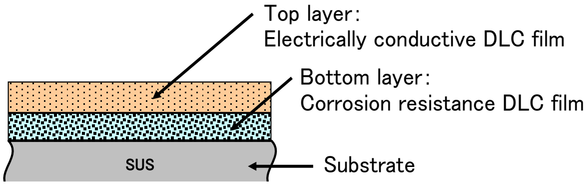


Figure 5. Bi-Layer film.

5.2. Corrosion resistance of electrically conductive DLC film

5.2.1. Anodic polarization curve Figure 6 shows anodic polarization curve with electrically conductive DLC and corrosion resistance DLC. Electrically conductive DLC is nano size film, it has grain boundary. and it is sp^2-rich. Therefore electrically conductive DLC film dissolves by applied voltage and has inferior corrosion resistance. Corrosion resistance DLC is sp^3-rich and has good corrosion resistance, current density is 10^{-6} A/cm^2.

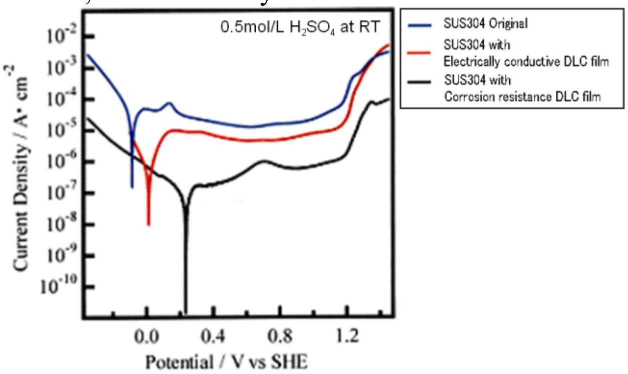
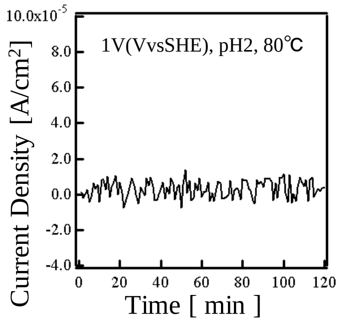


Figure 6. Anodic polarization curve with electrically conductive DLC and corrosion resistance DLC.

5.2.2. Electrochemical corrosion test Figure 7 shows potentionstatic test with H_2SO_4 pH2, 1Vvs SHE, 80℃ and metal dissolution. In potentionstatic test, current density is 10^{-6}A/cm^2. Fe dissolution is 0.02 ppm and very little. This film is superior to corrosion resistance.



Test condition	Metal contents [ppm]			
	Fe	Cr	Ni	Mo
1V, pH2, 80℃	0.02	0	0.002	0

Figure 7. Metal contents in ppm after immersion test in distilled water in test condition by ICP analyzer for test specimen.

6. Low Cost

6.1. high deposition rate equipment

We manufactured one unit to produce separators continuously in an in-line system consisted of many units in the future. In figure 8 shows conceptual diagram of PIAD(Plasma Ion Assisted Deposition) and figure 9 shows one unit of PIAD system. ICP source and mating box are attached in the front and the backside of equipment. Separator which is set up on 50cm square carrier is going and returning in right and left between ICP sources (space 10cm).Electrically conductive DLC is formed by heating, Ar-cleaning, N-ion implantation, and CH_4/C_2H_2 deposition in serial order.

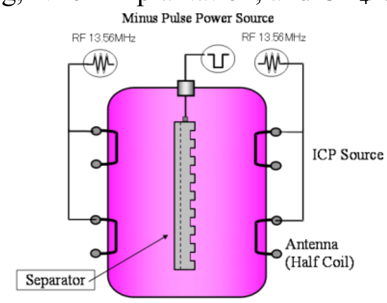


Figure 8. Conceptual diagram of PIAD.

Figure 9. One unit of PIAD system.

6.2. Deposition rate

Deposition rate is 5μm/hr by using ICP plasma with RF power 3kW, distance 15cm from ICP. Figure 10 shows deposition rate in case of distance 5cm from ICP. Deposition rate is proportional to the applied pulse voltage on substrate.

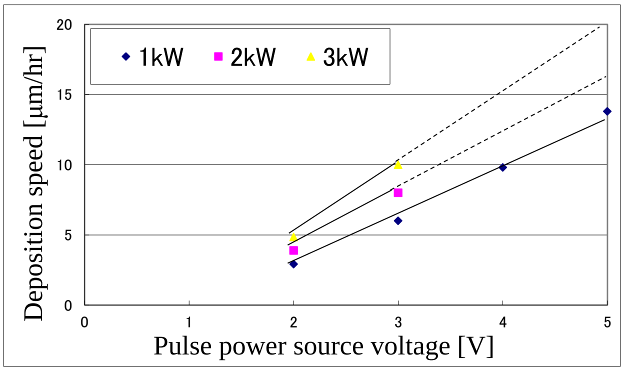


Figure 10. Deposition rate.

6.3. Reducing the coating cost

The coating cost depends on deposition rate. The faster deposition rate, the cheaper coating cost. In case of deposition rate 20μm/hr, film thickness 150nm, and substrate size A4, the coating cost is estimated to be 150yen.

7. Cell performance of electrical generation

7.1. Single Cell Performance

By using electrically conductive DLC coated stainless (SUS316L) steel separator, Electrical generation test of single cell for 1000 hours was carried out. The active electrode area was $25cm^2$. Table 1 shows detail test condition. Figure 11 shows single cell. Figure 12 shows cell performance of electrical generation.Figure13 shows change of cell resistance. These results showed same good characteristics in comparison with carbon separator and electrically conductive DLC coated stainless steel separator.

Table 1. Single cell test condition.

Temperature	80℃
Humidification	Saturated humidification
Gas condition	Hydrogen 136ml/min(70%) Oxygen 568ml/min(40%)
Current Density	$0.5\ A/cm^2$

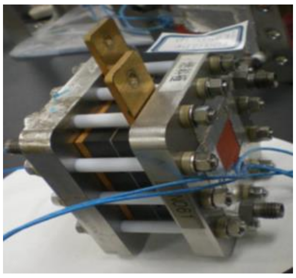


Figure 11. Single cell

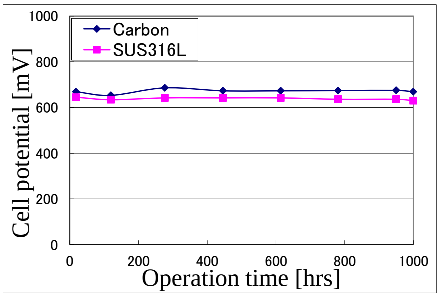


Figure12. Cell performance of electrical generation.

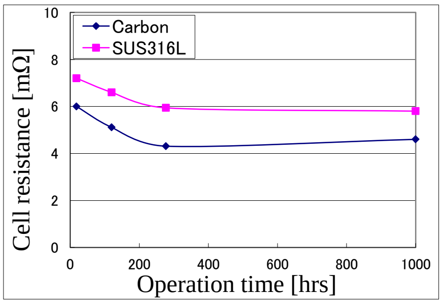


Figure13. Change of cell resistance.

7.2. *Stack Cell performance*

By using electrically conductive DLC coated stainless (SUS316L) steel separator stack of 5 cells. Electrical generation test for 1000 hours was carried out. The active electrode area was 167cm^2. Table 2 shows detail test condition. Figure 14 shows each cell performance of electrical generation. Figure 15 shows I-V performance before and after electrical generation. Each cell potential for a period of 1000 hours were very stable. And in I-V performance, same good polarization characteristics as carbon separator was gotten.

Table 2. Stack test condition.

Temperature	80℃
Humidification	Saturated humidification
Operation condition	WSS(Weekly Stop & Start)
Current Density	0.3 A/cm^2

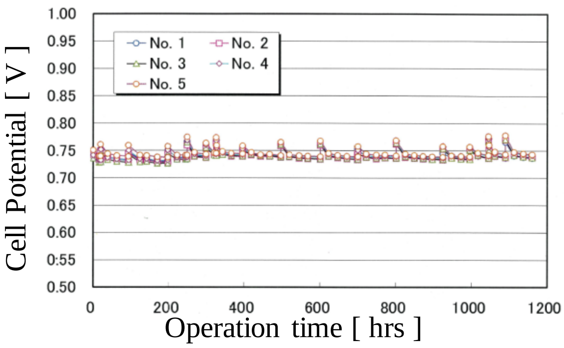


Figure14. Each cell potential for periods when cells were under load.

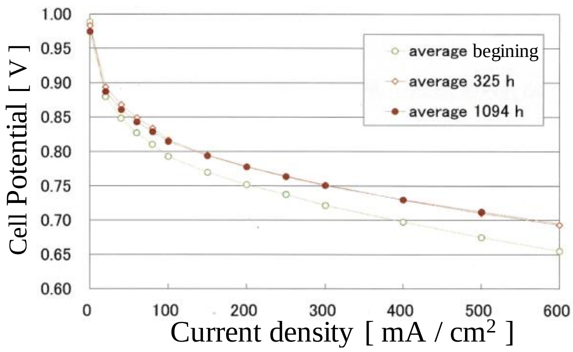


Figure15. Polarization characteristics.

8. Summary

Contact resistance is a few mΩ・cm^2 between GDL constructed with fuel electrode or air electrode, and electrically conductive DLC developed by technology of plasma based ion implantation and deposition .Also current density in corrosion test is less than 10^{-6}A/cm^2 and Fe metal contents after immersion test in distilled water test was 0.02 ppm under condition of 1V, pH2 H_2SO_4, 80℃. Deposition speed of over than 13μm/hr was gotten by using ICP plasma source. In that result possibility was found out that cost of electrically conductive DLC coated stainless steel separator was 150yen at 150nm DLC thin film in A4 size. It is expected that in future if electrically conductive 50nm DLC coated aluminum separator is developed, cost of separator is 50yen in A4 size.

9. References

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