

Synthesis of Diamond-like Carbon by PECVD on Different Substrates for Fuel Cell Applications

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Abstract— Lower cost, lighter weight, and higher electrical conductivity are among many advantages of using metallic bipolar plates (BPs) over the conventional graphitic materials in PEM fuel cell applications. In this study, diamond-like carbon (DLC) coatings are deposited on top surfaces of stainless steel (SS316) and Aluminum (Al5052) substrates via Plasma Enhanced Carbon Vapor Deposition (PECVD) in order to increase the durability. Further, the effect of different plasma power intensities and type of precursor gases, including methane (CH_4) and acetylene (C_2H_2), on the growth of DLC films is studied. Various ex-situ characterization techniques have been used to examine the strength of adhesion, morphologies, structures/compositions, and wettability of the DLC coatings. It is found that coatings produced from CH_4 gas show superior adhesion in comparison to those obtained from the C_2H_2 gas. Results indicate that higher deposition power intensity can produce more sp^3 bonds than sp^2 bonds. It is also determined that the type of the metallic substrates has predominant roles on the morphology of the DLC coatings. In addition, a moderate power intensity of 250 W results in desirable properties in DLC, including adhesion and wettability, compared to higher and lower plasma power intensities.

Keywords- Proton exchange membrane fuel cell; Bipolar plates; Diamond-like carbon.

I. INTRODUCTION

Bipolar plates (BPs) are one of the crucial components in polymer electrolyte membrane (PEM) fuel cells. They conduct electrons between adjoining cells, distribute reactants, facilitate water and heat management, and provide mechanical support. To accomplish these functions, bipolar plates must exhibit a number of desirable mechanical and surface properties. However, most commercial bipolar plates are made of heavy-

graphite and are considered to be the bulkiest and the second most-expensive component in the manufacture of PEM fuel cell stacks [1]. Due to the technical and cost requirements of BPs [1-3], metallic bipolar plates have received considerable attention to replace conventional graphite materials, but their durability inside the acidic PEM fuel cell environment is a challenging issue. Various surface modifications and protective coatings have been investigated, including [4]: noble metals such as gold [5], metal nitrides, and metal carbides. In the last decade, diamond-like carbon (DLC) has been considered an innovative candidate as a coating material for metallic BPs in PEM Fuel Cells [6]. In general, DLC can be formed as a thin film at relatively low deposition temperatures on metallic substrates. One of the most suitable DLC deposition techniques is Plasma Enhanced Chemical Vapor Deposition (PECVD) [7-9]. Carbon-based layer is deposited on stainless steel (SS304) via PECVD, and the coating sample presents the lower interfacial contact resistance in comparison to the SS304 without coating [10]. In other work, a 1 μm -thin layer of nickel is applied between the SS304 and carbon-base coating to improve adhesion [11]. The electrical conductivity of DLC film under different voltages is also reported [12]. Due to the potential advantages of using aluminum, different carbon-composite coatings for aluminum-base bipolar plates have also been investigated [13] [14]. However, information about DLC coating on the aluminum surfaces is limited. Therefore, the objective of this work is to investigate the effect of deposition parameters on the DLC properties for metallic-base substrates (stainless steel SS316 and aluminum Al5052).

II. EXPERIMENTAL AND CHARACTERIZATIONS

The DLC coating is deposited on Al5052 and SS316 substrates by using the fully automated INTLVAC's AUTOSYS control system. CH_4 and C_2H_2 are separately used as a precursor gas, and the carrier gas is argon. Different plasma power intensities of 70, 250, and 1000 W are applied in

order to investigate its impact of plasma power on the various characteristics of DLC coatings, whereas the argon gas percentage is fixed at 30% and the deposition time is a constant of 74 min. Various ex-situ characterization methods are employed to investigate the properties of the deposited films. Scanning electron microscopy is used to study the morphology of the prepared samples. Since the adhesion of the coating DLC films is one of the most challenging tasks of surface engineering, tape pull-off tests are used to check the coatings' adhesion to the metallic substrates. The morphology of the coated film is investigated by field emission-scanning electron microscopy (FE-SEM). Further, X-ray photoelectron (XPS) spectroscopy is commonly used for quantitative comparison between the molecule compositions existing on the coated surface. The DLC surface wettability indicates the hydrophobicity behavior of the BP coatings in order to determine whether they are suitable for PEM Fuel cell applications. The surface wettabilities of the DLC coatings on different Al5052 and SS316 samples are evaluated by measuring the static contact angle (θ), a characterization technique that uses a Ramé-Hart contact angle apparatus.

III. RESULTS

A. Adhesion

Table 1 summarizes the results of the adhesion tests between the DLC coatings on SS316 and Al5052 substrates, under the classifications as passed, failed, and partially failed. It shows the impact of varying the precursor gas between acetylene (C_2H_2) and methane (CH_4), and the power intensities between 70 W and 250 W, then 1000 W on the adhesion of the DLC coatings with the constant carrier gas (argon) percentage of 30 % and deposition time of 74 min.

TABLE 1. ADHESION TESTS OF DLC COATINGS ON SS316 AND AL5052 SUBSTRATES:

Deposition Parameters				Substrate Materials SS316	Substrate Materials Al5052
Power (W)	H/C gas	Ar (%)	Time (min)	Pass/Failed	Pass/Failed
70	C_2H_2	30	74	Failed	Failed
250	CH_4	30	74	Passed	Passed
1000	CH_4	30	74	Failed	Passed

It is observed that employing CH_4 gas can result in higher adhesion than C_2H_2 gas, especially with a moderate plasma power intensity of 250 for both Al5052 and SS316 substrates. This adhesion enhancement can be attributed to the different growth mechanisms of carbon composites between CH_4 gas and those produced from C_2H_2 . This difference occurs because DLC generated by using CH_4 produces more hydrogen in reaction, hence the etching reaction is developed during the deposition processes [15]. It is also noticed that increasing the plasma power intensity has a negative effect on the adhesion between the SS316 substrate and the coating. That is, a higher power intensity of 1000 W can result in poor DLC adhesion in comparison to 250 W. The poor adhesion at higher plasma power intensity is associated with a fast deposition rate as well as the growth of thicker DLC films. Consequently, the residual stress is higher inside the films due to the noticeable increase

in sp^3 bonding fraction, as will be discussed by the XPS analysis. On the other hand, varying the plasma power intensity has a negligible impact on the adhesion of the DLC coating on Al 5052 substrates. These results signify the roles of the metallic substrate on the adhesion property.

B. Morphology

Figure 1 (a-d) shows the surface morphologies of two different DLC coatings deposited on SS316 and Al5052 substrates at two different power intensities of 250 W and 1000 W. These images are taken from the top surface without using any gold coating. Figure 1 (a and b) are obtained using SS316, while 30 % of carrier gas is applied. These images show homogenous coverage, with the presence of big island-shaped regions (see the images with high magnification on top of the SEM images). Both surfaces are covered with dark and light particles, and this contrast can be attributed to the accumulation of particles with different electrical-conductivity properties. The DLC structure is basically amorphous carbon coordinated with sp^2 and sp^3 structures with different conductivity. It is expected that the sp^3 bond is responsible for the mechanical properties, while sp^2 bond presents the electronic properties. It can be seen that Figure 1 (a) is covered with a higher amount of darker particles, in comparison to Figure 1 (b). These results may suggest that using higher power in the PECVD process leads to a higher sp^3 structure. Further, Figure 1 (c and d) demonstrates the top surface of the coating on the Al5052 substrate under identical deposition conditions as those for Figure 1 (a and b). It can be observed that the two images have uniform and homogenous coverages with a stripe-like structure, which is considerably different than island-shaped structure in the SS316 substrate. These images clearly suggest that the types of substrate are a predominant factor in the morphology of the DLC coating. However, the deposition conditions also play important roles. For instance, Figure 1 (a) and (c) are prepared under identical conditions using different substrates, but the morphology of the samples is completely different (island versus stripe).

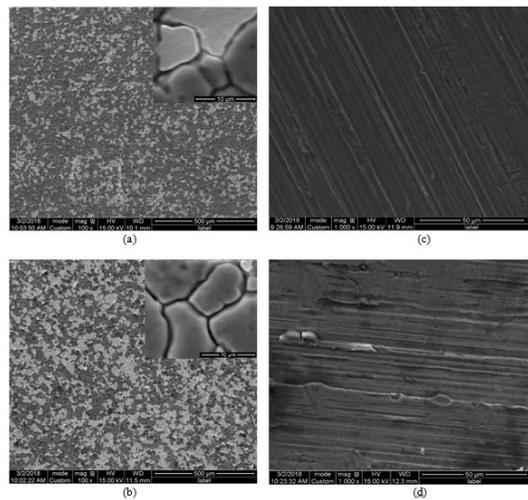


Figure 1. SEM images of coated films of DLC deposited SS316 substrates with plasma power intensity of (a) 250 W and (b) 1000 W, whereas (c) and (d) for coated films of DLC deposited on Al5052 substrates with plasma intensities of 250 and 1000 W, respectively

C. X-ray Analysis

Figures 1 (a) and (b) show the XPS spectra of DLC films deposited on SS316 substrates for plasma power intensities of 250 W and 1000 W, respectively, with a fixed carrier gas (argon) ratio of 30 %. The coating films are obtained under a deposition time of 74 min. Since the surface properties of the DLC films are strongly influenced by the ratios between the sp^3 and sp^2 of the carbon bonds, it can be expected that DLC with higher sp^2 carbon bonds will show graphene-like properties. It can be observed from Figure 1 (a-d) that the curve peak of DLC film deposited is deconvoluted into two components, which indicate the existences of different carbon bonds including sp^2 and sp^3 . It can be observed from Figure 1 (a) that about 81 % of the DLC coated film deposited on the SS316 is sp^2 carbon bonds. However, increasing the deposition power intensity to 1000 W lowered the amount of graphene-like bonds in the coating films by 15%. Further, figure 1 (c) shows curve peaks at 284 corresponds to the sp^2 binding energy on its spectrums, while the peak of DLC deposited with 1000 W has been shifted to the higher binding energy of 285 eV. It can be seen that the percentage of sp^2 is 70.9 % in the coated samples produced with 250 W, while the DLC coatings obtained with 1000 W contain 58.7 % sp^3 bonds. On the other hand, the second peak components occur at 286 eV, indicating the C=O bond in the coating film due to contamination. This suggests that a higher power intensity of 1000 W can result in incensing of the sp^3 bond in the DLC films. Further, these results may suggest that the metallic-substrate material and the deposition-power intensity can impact the deposited-film properties.

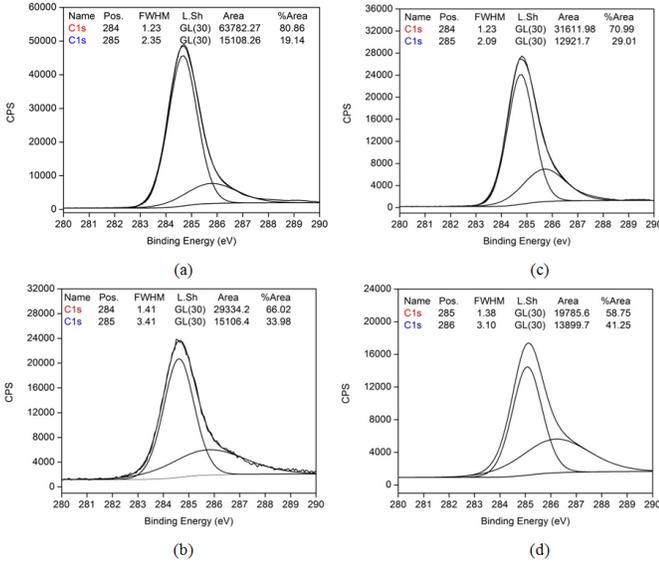


Figure 2. XPS analysis spectra of coating films of DLC with different power intensities (a) 250 W and (b) 1000 W deposited on SS316 substrates. Whereas coatings deposited on Al5052 substrates with power intensity of (c) 250 W and (d) 1000 W. Deposition conditions: CH₄ is a precursor gas, argon gas percentage of 30 %, time of 74 min, and voltage 120 V.

D. Wettability

Water management is a crucial issue inside operating PEM Fuel cells. The wettability and water repellency of the bipolar plates are important surface properties for water removal [16].

Therefore, the DLC coatings of the bipolar plate coatings surface must exhibit hydrophobicity behavior and water repellency. The surface wettabilities of the DLC coatings on different Al5052 and SS316 substrates are evaluated as in Table 2, showing the average values of the water contact angles (θ°) for the coated surface of SS316 and Al5052 substrates. The angles vary from 80° to 82° for the SS316 substrate, and from 76° to 91° for Al5052 under different plasma power intensities. Table 2 may suggest that the substrate material has a strong impact on the surface wettability characteristics. It demonstrates that increasing the deposition power intensity results in lowering the contact-angle values due to the diamond-like carbon structure [17]. This observation is found to be in good agreement with the XPS analysis discussed above, which showed that a higher percentage of sp^3 bonds in the coating with a higher power intensity of 1000 W in comparison to 250 W. Further, it is seen that coated films deposited with a lower power intensity of 250 W results in a higher contact angle of 91°.

TABLE 2: STATIC CONTACT ANGLE (θ) OF DLC DEPOSITED ON AL5052 AND SS316 SUBSTRATES

Deposition Parameters				Substrate Materials SS316	Substrate Materials Al5052
Power (W)	H/C gas	Ar (%)	Time (min)	Contact angle (°)	Contact angle (°)
250	CH ₄	30	74	82	91
1000	CH ₄	30	74	80	76

IV. CONCLUSIONS

The effect of power intensity on the carbon composite coatings deposited on aluminum (Al5052) and stainless steel (SS316) substrates has been investigated. Adhesion, SEM, XPS, and wettability measurements have been conducted to understand the characteristics and the compositions of the deposited coatings. It has been observed that coatings generated from CH₄ provide better adhesion than those coatings produced from C₂H₂ gas. Results suggest that the ratio between sp^2 and sp^3 bonds in the DLC coatings is strongly affected by the plasma power intensity. It has been found that a large percentage sp^3 (diamond-like) in the coating is produced at a high power density at the cost of the sp^2 bond (graphene-like). Therefore, the surface morphology and composition of the DLC coatings are strongly influenced by the deposition parameters and material of the metallic substrates. The coatings generated under power intensity of 250 W shows stronger adhesion with the metallic Al5052 and SS316 substrates than those produced higher power of 1000 W. Further, the DLC coatings deposited on metallic substrates demonstration hydrophobicity properties with a contact angle of between 80° of 90°.

REFERENCES

- [1] J. a. M. Spendelow, "Fuel Cell System Cost-2013", DOE Fuel and Cell Technologies Office Record, Record # 13012.
- [2] S. Chunhui, P. Mu, Y. Qin, and Y. Runzhang, "Studies on Preparation and Performance of Sodium Silicate/Graphite Conductive Composites," J. Comp. Mat., vol. 40, pp. 839-848, May 1, 2006. doi: 10.1177/0021998306061296.

- [3] D. J. L. Brett and N. P. Brandon, "Review of Materials and Characterization Methods for Polymer Electrolyte Fuel Cell Flow-Field Plates," *J. Fuel Cell Sci. Technol.*, vol. 4, pp. 29-44, Feb. 2006. doi: [10.1115/1.2393303](https://doi.org/10.1115/1.2393303).
- [4] S. Karimi, N. Fraser, B. Roberts, and F. Foulkes, "A Review of Metallic Bipolar Plates for Proton Exchange Membrane Fuel Cells: Materials and Fabrication Methods," *Adv. Mater. Sci. Eng.*, vol. 2012, p. 22, 2012. doi: [10.1155/2012/828070](https://doi.org/10.1155/2012/828070).
- [5] R. L. Borup and N. E. Vanderborgh, "Design and Testing Criteria for Bipolar Plate Materials for Pem Fuel Cell Applications," *MRS Proceedings*, vol. 393, p. 151, 1995. doi: [10.1557/PROC-393-151](https://doi.org/10.1557/PROC-393-151).
- [6] C. C. Wang, "Novel Structured Metal Bipolar Plates for Low Cost Manufacturing," Project ID# : FC105 2014.
- [7] R. Paul, S. Hussain, S Majumder, S Varma, and A. K. Pal, "Surface plasmon characteristics of nanocrystalline gold/DLC composite films prepared by plasma CVD technique," *Mater. Sci. Eng. B: Solid*, vol. 164, pp. 156-164, 2009. doi: [10.1016/j.mseb.2009.09.009](https://doi.org/10.1016/j.mseb.2009.09.009).
- [8] G. A. Viana, et al., "Diamond-like carbon deposited by plasma technique as a function of methane flow rate," *Diamond Relat. Mater.*, vol. 19, nos. 7-9, pp. 756-759, Jul. - Sept. 2010. doi: [10.1016/j.diamond.2010.01.043](https://doi.org/10.1016/j.diamond.2010.01.043).
- [9] D. Caschera, F Federici, S Kaciulis, L Pandolfi, A Cusmà, and G. Padeletti, "Deposition of Ti-containing diamond-like carbon (DLC) films by PECVD technique," *Mater. Sci. Eng. C*, vol. 27, nos. 5-8. pp. 1328-1330, Sept. 2007. doi: [10.1016/j.msec.2006.06.027](https://doi.org/10.1016/j.msec.2006.06.027).
- [10] T. Fukutsuka, T. Yamaguchi, S.-I. Miyano, Y. Matsuo, Y. Sugie, and Z. Ogumi, "Carbon-coated stainless steel as PEFC bipolar plate material," *J. Power Sources*, vol. 174, no. 1, pp. 199-205, Nov. 2007. doi: [10.1016/j.jpowsour.2007.08.096](https://doi.org/10.1016/j.jpowsour.2007.08.096).
- [11] C.-Y. Chung, S.-K. Chen, P.J. Chiu, M.-H. Chang, T.-T. Hung, and T.-H. Ko, "Carbon film-coated 304 stainless steel as PEMFC bipolar plate," *J. Power Sources*, vol. 176, no. 1, pp. 276-281, Jan. 2008. doi: [10.1016/j.jpowsour.2007.10.022](https://doi.org/10.1016/j.jpowsour.2007.10.022).
- [12] Md. K. Hassan, B. K. Pramanik and A., "Electrical Resistivities of the Diamond-Like Carbon Films Fabricated from Methane and Acetylene Using RF Plasma," *New Diamond Front. Carbon Technol.*, vol. 16, no. 4, pp. 211-219, Jan. 2006 .
- [13] J. R. Mawdsley, J. D. Carter, X. Wang, S Hiyogi, C. Q. Fan, R. Koc, and G. Osterhout, "Composite-coated aluminum bipolar plates for PEM fuel cells," *J. Power Sources*, vol. 231, no. 1, pp. 106-112, Jun. 2013. doi: [10.1016/j.jpowsour.2012.12.074](https://doi.org/10.1016/j.jpowsour.2012.12.074).
- [14] S.-J. Lee, C.H. Huang and Y.P. Chen., "Investigation of PVD coating on corrosion resistance of metallic bipolar plates in PEM fuel cell," *J. Mater. Process. Technol.*, vol. 140, nos. 1-3, pp. 688-693, Sept. 2003. doi: [10.1016/S0924-0136\(03\)00743-X](https://doi.org/10.1016/S0924-0136(03)00743-X).
- [15] M. Aksak S. Kir and Y. Selamet, "Effect of the growth temperature on carbon nanotubes grown by thermal chemical vapor deposition method." *J. Optoelectron. Adv. Mater. Symp.*, vol. 1 no. 3, pp. 281-284, 2009.
- [16] S. A. Shakhshira, Y. Wang, I. E. Alaefour, and X. Li, "The Influence of Channel Wettability on Two-Phase Flow and Polymer Electrolyte Membrane Fuel Cell Performance," *ECS Transactions*, vol. 42, pp. 109-115, 2012. doi: [10.1149/1.4705486](https://doi.org/10.1149/1.4705486).
- [17] J. Martí-González and E. Bertran, "Mechanical and Surface Characterization of Diamond-Like Carbon Coatings onto Polymeric Substrate," arXiv preprint arXiv:1509.08512, 2015.