Electrical Conductivity and Corrosion Resistance of DC Magnetron Sputtered Amorphous Carbon Films: Postprint

Authors: Zhang Haifeng, Zhang Dong, Li Xiaowei, Lu Congda, Peiling Ke, Wang Aiying

Date: 2023-03-18T00:00:00+00:00

Abstract

Conductive amorphous carbon films were prepared on 304 stainless steel substrates using direct current magnetron sputtering technology, with emphasis on investigating the influence of substrate bias voltage on the microstructure, electrical conductivity, and corrosion resistance of the amorphous carbon films. The results show that, compared with pure stainless steel bipolar plates, both the electrical conductivity and corrosion resistance of stainless steel surfaces modified by amorphous carbon films are significantly improved. When the substrate bias voltage is -200 V, the sp2 content of the amorphous carbon film is the highest under the typical assembly pressure of proton exchange membrane fuel cells (1.5 MPa), enabling the modified stainless steel bipolar plates to have the lowest contact resistance (16.65 mΩ · cm2); in a corrosive solution simulating the working environment of proton exchange membrane fuel cells, the corrosion potential of the coated stainless steel plates is significantly increased, and the corrosion current is significantly decreased. Especially under a bias voltage of -200 V, the film exhibits the best compactness, with a corrosion potential of 0.25 V and a corrosion current density of 1.22$×10^{-8}$ A/cm2, demonstrating the best corrosion resistance.

Full Text

Electric Conductivity and Corrosion Resistance of Amorphous Carbon Films Prepared by Direct Current Magnetron Sputtering on 304 Stainless Steel

ZHANG Haifeng[1],[2], ZHANG Dong[2], LI Xiaowei[2], LU Congda[1], KE Peiling[2], WANG Aiying[2],*

[1]Zhejiang University of Technology, Hangzhou 310014, China
[2]Key Laboratory of Marine Materials and Related Technologies, Zhejiang Key Laboratory of Marine Materials and Protective Technologies, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, China

Supported by National Natural Science Foundation of China (Nos. 51175472 & 51522106), Ningbo Municipal Natural Science Foundation (No. 2015A610083), and Ningbo Municipal Key Technologies R&D Program (No. 2014B10032).

Manuscript received January 14, 2015; in revised form April 9, 2015. To whom correspondence should be addressed, Tel: (0574) 8668517; E-mail: aywang@nimte.ac.cn

Abstract

Conductive amorphous carbon films were deposited on 304 stainless steel (SS304) by conventional direct current magnetron sputtering, with particular focus on investigating the effects of substrate bias on the microstructure, electrical conductivity, and corrosion resistance of the films. The results demonstrate that both electrical conductivity and corrosion resistance are significantly improved for carbon-coated stainless steel compared to untreated substrates. Specifically, when the substrate bias was -200 V, the films exhibited the highest sp^2 content under the typical assembly pressure of proton exchange membrane fuel cells (1.5 MPa), yielding the lowest contact resistance of 16.65 m$\Omega\cdot$cm^2. In simulated PEM fuel cell corrosive environments, the coated stainless steel showed substantially increased corrosion potential and decreased corrosion current. The films deposited at -200 V bias demonstrated optimal compactness, achieving a corrosion potential of 0.25 V and a corrosion current density of 1.22$×10^{-8}$ A/cm^2, indicating the best corrosion resistance.

Keywords: inorganic non-metallic materials, PEM fuel cells, amorphous carbon films, magnetron sputtering, contact resistance, corrosion resistance

Introduction

Bipolar plates are critical components in proton exchange membrane fuel cells (PEMFCs), serving to separate oxidant and reductant, facilitate water drainage, ensure uniform temperature distribution, isolate individual cells within the stack, and collect/conduct current [1]. Traditional graphite bipolar plates exhibit excellent conductivity and corrosion resistance but suffer from high cost and brittleness. Stainless steel offers superior electrical and thermal conductivity, high mechanical strength, and good formability, making it an ideal bipolar plate material. However, its native surface oxide layer creates high contact resistance, and corrosion under fuel cell operating conditions can leach nickel, chromium, and iron components, contaminating electrodes and degrading fuel cell performance and lifespan. Surface modification via thin film technology is therefore essential to enhance service performance and enable large-scale application.

Zhang et al. [2] deposited TiN coatings on 304 stainless steel using both magnetron sputtering and pulsed bias arc ion plating, achieving good corrosion resistance and low contact resistance. However, the high electrode potential of TiN coatings relative to the substrate creates galvanic couples that accelerate substrate corrosion [3, 4]. Amorphous carbon films, with their dense structure, favorable conductivity, and corrosion resistance, combined with the high mechanical strength of metallic substrates, represent an excellent choice for bipolar plate surface modification. Show [5, 6] deposited carbon films on Ti bipolar plates at various temperatures, achieving a resistivity of $10^{-3}\ \Omega\cdot\mathrm{cm}$ at 600°C; fuel cells assembled with these coated bipolar plates delivered 1.4 times the output power of uncoated Ti plates. Shen et al. [7] used closed-field unbalanced magnetron sputtering to deposit 3 m dense, uniform amorphous carbon films on 316L stainless steel with high sp^2 content, achieving contact resistance superior to graphite bipolar plates and significantly improved corrosion resistance. Peng et al. [8] employed the same method on 304 stainless steel, demonstrating that amorphous carbon films provide excellent chemical stability and substantially enhance fuel cell performance.

Amorphous carbon films constitute a broad class of disordered carbon materials whose structure and properties are closely related to deposition methods and process parameters. Direct current magnetron sputtering offers low cost, operational convenience, and suitability for large-area uniform coating, making it an ideal method for preparing low-cost, high-performance conductive carbon films for bipolar plate modification. This study employs DC magnetron sputtering to deposit amorphous carbon films on 304 stainless steel substrates, investigating the influence of substrate bias on film structure, conductivity, and corrosion resistance.

---

1. Experimental Methods

Amorphous carbon films were deposited under various bias voltages using a magnetic filtered cathodic arc hybrid sputtering system. Substrate materials included glass, silicon wafers, and mirror-polished 304 stainless steel sheets (1 mm thick, 30 mm × 30 mm). Prior to deposition, substrates were ultrasonically cleaned in acetone for 15 minutes, dried, and mounted in the chamber. After evacuation to 4$×10^{-3}$ Pa, Ar gas was introduced to maintain a pressure of 1 Pa, and the substrates were etched by Ar ion glow discharge at -300 V bias for 30 minutes. A Cr transition layer was then deposited by activating a chromium target (99.99% purity) DC power supply at 3 A sputtering current, -100 V substrate bias, 50 mL/min Ar flow rate for 10 minutes. Subsequently, a graphite target (99.99% purity) DC power supply was activated, and carbon films were deposited at substrate biases of -50 V, -200 V, and -350 V, with 3 A sputtering current, 50 mL/min Ar flow rate for 60 minutes. During deposition, the Ar partial pressure was 0.28 Pa, and substrates were rotated at a constant speed before the sputtering target to ensure coating uniformity.

Film microstructure was analyzed using a RENISHAW inVia confocal Raman spectrometer with a 532 nm laser wavelength. Surface and cross-sectional morphology were examined using an S-4800 field emission scanning electron microscope (FESEM). Three-dimensional surface topography and roughness were measured using a Dimension3100V scanning probe microscope (SPM). Surface hydrophobicity/hydrophilicity was evaluated using an OCA20 contact angle measurement system. Film resistivity was determined using a CRESBOX four-point probe tester. Contact resistance between stainless steel bipolar plates and gas diffusion layers was measured following the method in reference [9], using Toray 060 carbon paper and 30 mm × 30 mm samples. The test configuration [Figure 1: see original paper] placed the sample between two carbon paper sheets supported by copper plates. A constant 1 A current was applied, compaction force was controlled programmatically using a CMT5105 electronic universal testing machine, and voltage variations across the circuit were measured with a precision multimeter at different pressures.

Electrochemical corrosion tests were conducted at room temperature using a three-electrode system on an AUTOLAB workstation, with a platinum counter electrode, saturated calomel electrode (SCE) reference, and surface-modified 304 stainless steel working electrode. Samples were sealed with hot-melt adhesive, exposing only a 1 cm × 1 cm test area. Potentiodynamic scans ranged from -0.7 V to 1.0 V at 0.5 mV/s in a corrosion solution of 0.5 mol/L H_2SO_4 + 5$×10^{-6}$ HF.

2.1 Film Surface Morphology

Surface and cross-sectional morphologies of carbon films prepared under different biases are shown in [Figure 2: see original paper]. Under otherwise identical parameters, film thickness remained relatively constant at 650$±$30 nm, with the Cr transition layer approximately 250 nm thick. At -200 V bias, the carbon film exhibited optimal density and uniformity. However, when bias increased to -350 V, surface particles coarsened and the structure became porous. This occurs because increasing substrate bias enhances ion bombardment energy; moderate bias improves film densification, but excessive bias induces resputtering and local structural relaxation, resulting in a loose film structure.

AFM topography images of amorphous carbon films deposited under various biases are presented in [Figure 3: see original paper]. Surface roughness was calculated from randomly selected 3 µm × 3 µm areas. The films demonstrated good smoothness, with surface roughness decreasing from 5.06 nm to 4.61 nm as bias increased from -50 V to -200 V, attributed to enhanced surface diffusion filling voids and defects. Further bias increase to -350 V caused surface particle coarsening due to high-energy bombardment, increasing Ra to 5.58 nm, consistent with SEM observations.

2.2 Carbon Film Structure

Typical amorphous carbon Raman spectra exhibit two peaks after Gaussian fitting at approximately 1350 cm^{-1} and 1560 cm^{-1}, designated D and G peaks [10, 11, 12], both arising from sp^2 structures. The G peak corresponds to sp^2 cluster structures from C-C bond stretching vibrations in carbon rings and chains, while the D peak corresponds to disordered microcrystalline graphite sp^2 structures from carbon ring breathing vibrations [13]. Gaussian fitting yielded the D-to-G peak intensity ratio (I_D/I_G), G peak position (Pos(G)), and G peak full width at half maximum (FWHM(G)), shown in [Figure 4: see original paper]. All deposited films displayed characteristic amorphous carbon Raman features. As substrate bias increased from -50 V to -350 V, I_D/I_G and Pos(G) initially increased then decreased, while structural disorder (FWHM(G)) from bond length and angle variations showed the opposite trend. These results indicate that sp^2 content first increased then decreased with bias, reaching maximum at -200 V.

2.3 Film Conductivity

[Figure 5: see original paper] shows the resistivity of amorphous carbon films on glass substrates measured by the CRESBOX four-point probe. All films exhibited good conductivity, with resistivity increasing from 2.58$\times10^{-6}$ $\Omega\cdot$m to 3.16$\times10^{-6}$ $\Omega\cdot$m as bias increased from -50 V to -350 V, all superior to conventional graphite (8$\times10^{-6}$ $\Omega\cdot$m).

Low contact resistance and high conductivity are crucial for minimizing ohmic losses and improving power output efficiency in fuel cell stacks. Contact resistance is primarily influenced by contact area between the sample and carbon paper and the sample' s surface conductivity. PEMFC stacks typically operate at compaction forces around 150 N/cm^2, requiring contact resistance below 20 m$\Omega\cdot$cm^2 [14]. [Figure 6: see original paper] presents contact resistance between uncoated and carbon-coated 304 stainless steel and Toray 060 carbon paper under various compaction forces. Contact resistance decreases with increasing force due to larger contact area. Uncoated stainless steel exhibits high contact resistance due to its passive surface layer. Carbon film deposition significantly reduces contact resistance, dramatically improving surface conductivity. Notably, at -200 V bias, contact resistance reaches 16.65 m$\Omega\cdot$cm^2, an 87% reduction compared to untreated stainless steel, attributed to the highest sp^2 content at this bias.

2.4 Film Corrosion Resistance

Potentiodynamic polarization curves in simulated PEM fuel cell environment (0.5M H_2SO_4 + 5×10^{-6} F^-) for uncoated and carbon-coated stainless steel are shown in [Figure 7: see original paper]. Uncoated stainless steel exhibits low corrosion potential (-0.35 V) and high passive current density (~10^{-5} A/cm^2) due to passive film breakdown at grain boundaries and dislocations. The Cr transition layer alone enhances film-substrate adhesion and provides protection, yielding a corrosion potential of -0.30 V and reduced passive current density of 5×10^{-6} A/cm^2. The corrosion mechanism involves pitting through pinhole defects in the Cr layer, as illustrated in [Figure 8: see original paper]. Depositing a dense, uniform amorphous carbon film atop the Cr layer significantly improves corrosion resistance due to the carbon film’ s excellent chemical inertness. As bias increased from -50 V to -200 V, corrosion potential rose to 0.25 V and corrosion current density decreased to 1.22×10^{-8} A/cm^2, demonstrating optimal corrosion resistance from enhanced film densification that effectively blocks corrosive species. At -350 V bias, excessive ion bombardment energy created a porous structure with defects that served as corrosion pathways, accelerating attack. Thus, moderate bias is a critical parameter for achieving optimal film density.

2.5 Film Surface Hydrophobicity

Bipolar plate hydrophobicity significantly affects water management efficiency in fuel cell stacks [15]. The proton exchange membrane requires humidification for adequate proton conductivity, while the redox reaction generates liquid water, exposing bipolar plates to continuous gas-water contact. Inadequate water removal causes electrode flooding and accelerates corrosion. Higher contact angles facilitate water removal and improve water management [16]. [Figure 9: see original paper] shows contact angle measurements before and after coating. The 304 stainless steel-water contact angle is 69.4°, which increases after carbon film deposition. At -200 V bias, the contact angle reaches a maximum of 89.5°, beneficial for water management. Solid surface hydrophobicity depends on surface energy and microstructure [17]. The prepared amorphous carbon films are relatively smooth, making surface energy the dominant factor. Surface energy is primarily determined by its polar component, which decreases with increasing sp^2 content due to weak polarity from dangling bonds [17, 18]. The -200 V bias films, having the highest sp^2 content, exhibit the lowest surface energy and optimal hydrophobicity.

Conclusions

1. Uniform, dense amorphous carbon films can be deposited on 304 stainless steel substrates by DC magnetron sputtering. At -200 V bias, the films achieve optimal density and uniformity.
2. Carbon film modification substantially reduces bipolar plate contact resistance. Under PEMFC stack compaction force of 150 N/cm^2, films deposited at -200 V bias exhibit a contact resistance of 16.65 $m\Omega \cdot cm^2$, representing an approximately 87% reduction compared to untreated 304 stainless steel.
3. Carbon-coated stainless steel bipolar plates demonstrate excellent corrosion resistance. At -200 V bias, the corrosion potential reaches 0.25 V with minimum corrosion current density of 1.22$×10^{-8}$ A/cm^2, attributed to the most compact film structure at this bias.
4. Coated stainless steel surfaces show increased water contact angles, promoting fuel cell water management.

References

1. ZHANG Haifeng, YI Baolian, HOU Ming, QIAO Fengtong, ZHANG Huaming, Materials for bipolar plates in proton-exchange membrane fuel cells and their preparation, Chinese journal of power sources, 27(2), 129(2003) (张海峰, 衣宝廉, 侯明, 乔凤桐, 张华民, 质子交换膜燃料电池双极板的材料与制备, 电源技术, 27(2), 129(2003))
2. Dongming Zhang, Liangtao Duan, Lu Guo, Wei-Hsing Tuan, Corrosion behavior of TiN-coated stainless steel as bipolar plate for proton exchange membrane fuel cell, Int.J.Hydrogen Energy, 35(8), 3721(2010)
3. S. Rudenjaa, C. Leygrafa, J. Pana, P. Kulub, E.Talimetsc, V.Miklid, Impedance spectroscopy of PVD- TiN coatings on mild steel and AI-SI316 substrates, Surface and Coatings Technology, 76-77, 615 (1995)
4. S. Rudenjaa, C. Leygrafa, J. Pana, P. Kulub, E.Talimetsc, V.Miklid, Duplex TiN coatings deposited by arc plating for increased corrosion resistance of stainless steel substrates, Surface and Coatings Technology, 114(2-3), 129(1999)
5. Show Y. Electrically conductive amorphous carbon coating on metal bipolar plates for PEFC, Surf Coat Technology, 202(4-7), 1252 (2007)
6. Show Y. Electrically conductive amorphous carbon coating on metal bipolar plates for PEFC, Surf Coat Technology, 202(4-7), 1252 (2007)
7. K. Feng, Y. Shen, H.L. Sun, D.G. Liu, Q. An, X. Cai, Paul K. Chu, Conductive amorphous carbon-coated 316L stainless steel as bipolar plates

in polymer electrolyte membrane fuel cells, Int.J.Hydrogen Energy, 34(16), 6771(2009)

8. Peiyun Yi, Linfa Peng, Tao Zhou, Hao Wu, Xinmin Lai, Development and characterization of multilayered Cr- C/a- C: Cr film on 316L stainless steel as bipolar plates for proton exchange membrane fuel cells, J. Power Sources, 230(15), 25(2013)
9. Heli Wang, Mary Ann Sweikart, John A Turner, Stainless steel as bipolar plate material for polymer electrolyte membrane fuel cells, J. Power Sources, 115(2), 243(2003)
10. K. W. R. Gilkes, S. Prawer, K. W. Nugent, J. Robertson, H. S. Sands, Y. Lifshitz, X. Shi, Direct quantitative detection of the sp3 bonding in diamond-like carbon films using ultraviolet and visible Raman spectroscopy, J Appl Phys, (87), 7283(2000)
11. A. C. Ferrari, J. Roberson, Resonant Raman spectroscopy of Disordered amorphous and diamond like carbon, Phys Rev B, 64, 075414 (2001)
12. A. C. Ferrari, J. Robertson, Interpretation of Raman spectra of disordered and amorphous carbon, Phys Rev B, 61(20), 14095(2000)
13. A. C. Ferrari, J. Robertson, Interpretation of Raman spectra of disordered and amorphous carbon, Phys Rev B, 61(20), 14095(2000)
14. E. A Cho, U. -S Jeon, H. Y Ha, S. -A Hong, I. -H Oh, Characteristics of composite bipolar plates for polymer electrolyte membrane fuel cells, J. Power Sources, 125(2), 178(2004)
15. Peiyun Yi, Linfa Peng, Tao Zhou, Hao Wu, Xinmin Lai, Development and characterization of multilayered Cr- C/a- C: Cr film on 316L stainless steel as bipolar plates for proton exchange membrane fuel cells, J. Power Sources, 230(15), 25(2013)
16. E. A Cho, U. -S Jeon, H. Y Ha, S. -A Hong, I. -H Oh, Characteristics of composite bipolar plates for polymer electrolyte membrane fuel cells, J. Power Sources, 125(2), 178(2004)
17. JIANG Lei, Nanostructured materials with superhydrophobic surface from nature to biomimesis, Chemical Industry and Engineering Progress, 22(12), 1258(2003) (江雷，从自然到仿生的超疏水纳米界面材料，化工进展，22(12), 1258(2003))
18. Y. Zhou, B. Wang, X. Song, E. Li, G. Li, S. Zhao, H. Yan, Control over the wettability of amorphous carbon films in a large range from hydrophilicity to super-hydrophobicity, Applied Surface Science, 253, 2690(2006)

Note: Figure translations are in progress. See original paper for figures.