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Properties of carbon film deposited on stainless steel by close field unbalanced magnetron sputter ion plating

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ABSTRACT

Carbon films are deposited on 304 stainless steel (SS304) by close field unbalanced magnetron sputter ion plating using different substrate bias voltages and target currents to improve the corrosion resistance and electrical conductivity of bipolar plates made of SS304 in proton exchange membrane fuel cells (PEMFCs). The surface morphology, Raman scattering spectra, corrosion resistance, interfacial contact resistance (ICR), and contact angle with water of the carbon films are determined. A dense carbon film is produced on the SS304 by this technique and the corrosion resistance is improved significantly. The ICR value diminishes drastically and water contact angle increases after deposition. In addition, the passive current density in the simulated PEMFC environment decreases initially, increases as the substrate bias voltage is increased, and drops with decreasing target current. As the substrate bias is increased, the ICR between the carbon film and carbon paper exhibits an initial diminishing trend and then increases, but the effect of the target current on the ICR is not as substantial as that of the bias voltage.

1. Introduction

Although magnetron sputtering [1] is widely used in surface engineering of functional materials, the main limitation is the reduced ion current impacting the substrate at large distances. An unbalanced magnetron field [2] enables the plasma to flow towards the substrates thereby allowing some of the secondary electrons produced during sputtering to follow the field lines resulting in additional ionizing collisions. Close field unbalanced magnetron sputter ion plating (CFUBMSIP) was invented by Teer [3] in 1996. In this technique, the closely linked magnetic field lines trap all the electrons generated in the system to further increase the ion current density surrounding the substrates to about 7 mA cm^{-2} [4], which is one hundred times higher than that in traditional magnetron sputtering. Therefore, ion bombardment on the substrates becomes more intense enabling the deposition of dense and adherent coatings with less defects.

According to previous studies [5–8], carbon films with a large sp^2 percentage prepared by chemical or physical vapor deposition have high electrical conductivity, chemical inertness, and hydrophobicity. However, in bipolar plate applications, the properties need to be further improved. Bipolar plates account for a large percent of the mass and cost [9] in the proton exchange membrane fuel cell (PEMFC) stack in electric vehicles [10]. The ideal bipolar plates should possess high electric conductivity, good corrosion resistance, high hydrophobicity, high mechanical strength, high gas impermeability, light weight, and low cost [11].

The properties of the carbon films fabricated by CFUBMSIP are affected by deposition parameters such as the substrate bias voltage, target current, gas pressure, as well as substrate temperature. In particular, the former two factors play an important role in the film performance. There have been studies on the influence of the substrate bias voltage on the microstructure and mechanical properties [12–15], corrosion resistance [16–18], and electrical conductivity [19–21], but the relationship between the corrosion resistance and electrical conductivity with the substrate bias voltage has not been studied. Furthermore, there have been few studies concerning the influence of the target current which is a very important deposition parameter. In our previous study, carbon-coated 304 stainless steel (SS304) samples were found to have high corrosion resistance, low interfacial contact resistance (ICR), and hydrophobicity and is thus a promising candidate as bipolar plates [8]. In this work, carbon films are produced by CFUBMSIP at different substrate bias voltages and target currents, and the effects of these deposition parameters on film properties such as the density, corrosion resistance, electrical conductivity, and surface hydrophobicity are investigated.

2. Experimental details

2.1. Preparation and characterization

The SS304 substrates were polished with No. 2000 SiC waterproof abrasive papers, cleaned with acetone in an ultrasonic cleaner for

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Table 1
Deposition parameters and thickness of the carbon films.

Sample	Bias voltage (V)	Target current (A)	Thickness of transition layer (μm)	Thickness of surface layer (μm)
S1	−20	7	1.14	1.89
S2	−60	7	0.88	2.06
S3	−100	7	1.03	1.93
S4	−150	7	1.07	2.25
S5	−60	5	0.96	1.46
S6	−60	3	0.81	1.87

15 min, and dried. The carbon films were deposited on the substrates on a CFUBMSIP system consisting of two 99.99% pure graphite targets and two 99.99% pure chromium targets. Before deposition, the substrates were sputter-cleaned by a plasma at −500 V to obtain an active surface to improve the adhesion between the substrate and coating. To produce a uniform film, the substrates were rotated at 2.5 r min^{-1}. A chromium carbide was first deposited onto the substrates as a transition layer to enhance adhesion using all four targets. Afterwards, the carbon film was deposited using the two graphite targets at substrate bias voltages of −20, −60, −100, and −150 V while the target current was fixed as 7 A. After determining the optimal bias voltage based on the performance the carbon films, the carbon films were deposited using target currents of 5 and 3 A.

The thickness of the carbon film prepared under each set of conditions was fixed at approximately 3 μm by using the proper deposition time. The thickness of the carbon film on the SS304 was measured on a crater machine (BC-2, Teer Coatings, Ltd.) [22] and the important deposition parameters and carbon film thicknesses are listed in Table 1. The surface morphology of the carbon films were examined by high-resolution field emission scanning electron microscope (SEM) (Sirion 200, FEI) and Raman scattering spectra were obtained on a dispersive Raman microscope (Senterra R200-L, Bruker Optics).

2.2. Electrochemical tests

Electrochemical measurements were conducted on an advanced electrochemical system (PARSTAT 2273, Princeton Applied Research, a subsidiary of AMETEK, Inc.) using a three-electrode cell. A saturated calomel electrode (SCE) was the reference electrode, a graphite rod served as the counter electrode, and the samples were the working electrode. Unless otherwise stated, the potential was referenced to the SCE. To simulate the operation conditions of the PEMFC, all the electrochemical experiments were conducted in a 0.5 M H_2SO_4 + 2 ppm HF solution at 80 °C. Because bipolar plates in the PEMFC are exposed to air/oxygen on one side and hydrogen gas on the other side, the solution was purged with either pressurized air (to simulate the PEMFC cathode environment) or hydrogen (to simulate the PEMFC anode environment) during the measurements, as reported by Fukutsuka et al. [5] and Choi et al. [23]. To ensure the electrochemical stability of the system, the open circuit potential (OCP) was monitored for 1 h before the potentiodynamic tests and to clarify the electrochemical behavior, the potentiodynamic curves were acquired at a scanning rate of 1 mV-s^{-1}.

2.3. Interfacial contact resistance

The ICR between the gas diffusion layer and bipolar plate is an important property of bipolar plates in PEMFCs and significantly affects the power output of the fuel cell stack. The ICR between the carbon-coated SS304 and conductive carbon paper (Toray TGP-H-060) was evaluated

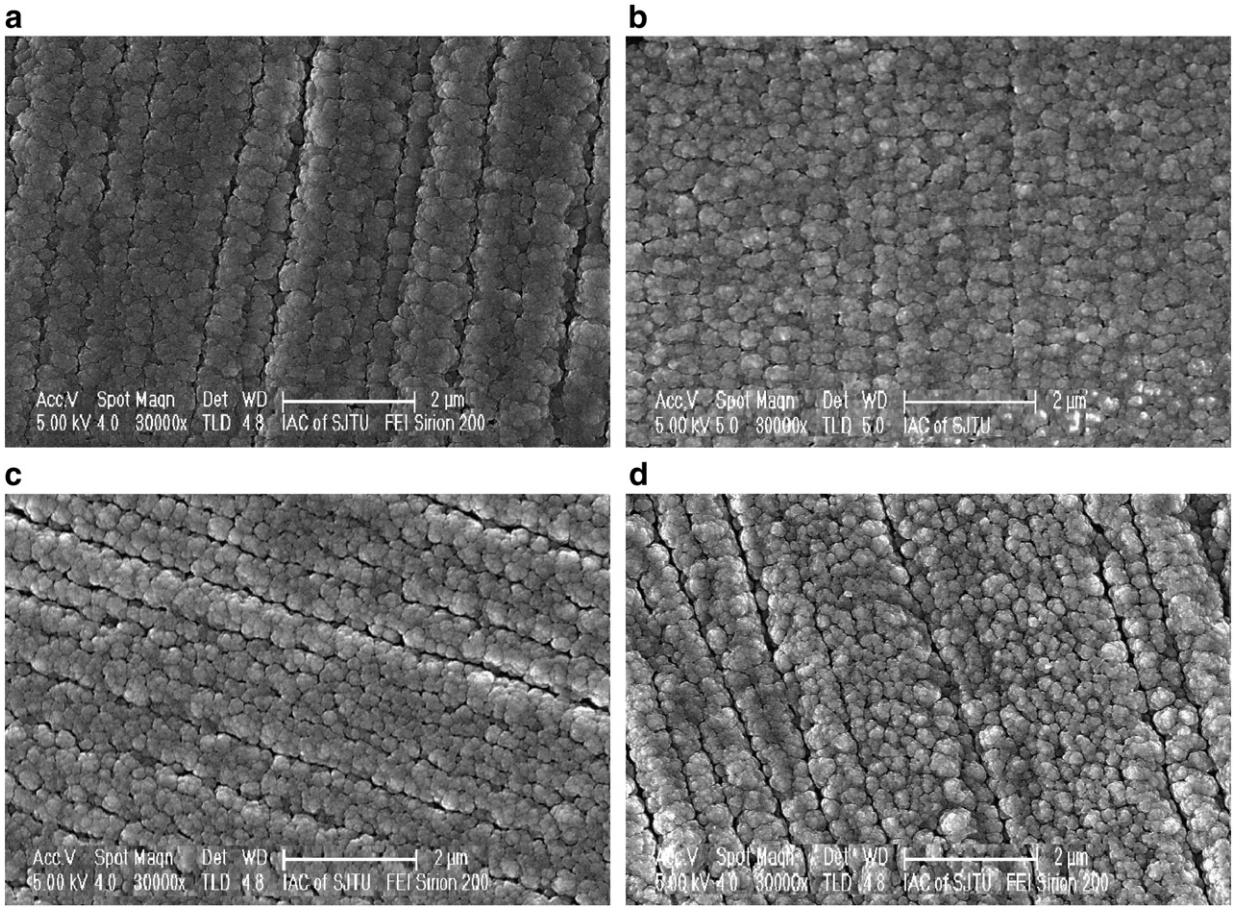

Fig. 1. SEM images of the surface of carbon films sputtered using a target current of 7 A and substrate bias voltages of (a) −20 (S1), (b) −60 (S2), (c) −100 (S3) and (d) −150 V (S4).