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Electrochemical characteristics of fluorine-doped tin oxide film coated on stainless steel bipolar plates

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ABSTRACT

In order to improve the interfacial contact resistance (ICR) and corrosion resistance of STS316 bipolar plates of PEMFCs, after surface pretreatment at mild plasma condition, the fluorine-doped tin oxides (FTO) thin films were deposited by electron cyclotron resonance-metal organic chemical vapor deposition. The mild plasma pre-treatment of the bipolar plate substrate before its coating with the FTO film has rendered a higher efficiency to the pertinent fuel cell, which can be attributed to a smooth charge transfer at the interface of the plate and the film due the removal of fine impurities on the substrate that could not be done just by washing. The deposition of FTO as a protect layer of fuel cell electrode after mild plasma pre-treatment improved the electrochemical stability. In our experimental range, with the increases in microwave power up to 1000 W, both of the corrosion resistance and ICR significantly decreased, however, those values sharply increased above 1100 W due to the crack and unstable film formation with the void space. Selecting the optimized value of the microwave power appeared to be the critical process step on the formation of the corrosion-protective layer for bipolar plates.

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) gained the most interests in the recent emerging energy devices because of their excellent stabilities and capabilities to generate high energy efficiency power as the electricity sources [1,2]. Like any other type of fuel cell systems, PEMFCs are composed of anode, cathode, membrane, and fuel sources. In particular, the bipolar plate (BP) plays a very important role to improve the energy efficiency of the overall PEMFC system [3,4].

There are several requirements for the BP materials, in order to satisfy the fuel cell systems, such as low cost, lightweight and low volume, mechanical and chemical stability, and low contact resistance. Presently, the most common materials to be used to fabricate BP are austenite stainless steels (STS316) [5]. In general, STS316 is chosen to make the BP, due to their high power density, lower cost, and their transport properties to easily supply the gas to the fuel cell [6–8]. There are other important parameters for the BP materials such as the contact and corrosion resistance in order to enhance the energy efficiency during PEMFC operation. The STS316 has practically low contact resistance and excellent corrosion resistance for the PEMFC system [9]. When the STS316 is incorporated for the BP materials, there is a significant influence for the PEMFC system, especially to carry out the strong hydro-acid reactions. High interfacial contact and corrosion resistance are sustained because of the oxidation state on the STS316 surface [10]. With the coating on the STS316 surface, we can further control these properties.

In this work, we carried out the deposition of fluorine-doped tin oxide (SnOx:F–FTO) film onto STS316 substrates, prepared by the electron cyclotron resonance–metal organic chemical vapor deposition (ECR–MOCVD) in order to enhance the contact and corrosion resistance of BP material. With our equipment, the high density coating of FTO films was possible where the FTO film play as an electrical conductor followed by the plasma treatment as the surface improver. Here, we observed the micromorphology and microstructure of the FTO film coated on STS316 under a strong hydro-acid environment. In addition, we investigated the electrochemical parameters of the FTO thin film such as the morphology, crystal structure, chemical binding, ICR, and corrosion resistance.

2. Experimental

The ECR–MOCVD system as the deposition apparatus was described in detail in our previous work [11]. Microwave sources with the frequency of 2.45 GHz under a magnetic flux density of 875 G were introduced through a rectangular guide into the plasma chamber to generate

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the plasma at low temperature (<80 °C). A 1.0 × 1.0 cm^2 SUS316 substrate was used and placed at a rotating substrate holder during the FTO film deposition. Before the depositions, we cleaned the SUS316 surface with the H_2/Ar plasma in order to increase the deposition efficiency between the FTO film and the surface of SUS316 and to tightly bond the FTO film with the BP surface [9,10]. This treatment lasted for 10 min prior to the deposition. The precursor gases, tin and fluorine, were obtained from the tetra-methyl tin (TMT) and sulfur hexafluoride (SF_6), respectively. The TMT was then introduced into the deposition chamber using argon as a carrier gas. The argon gas flow rate of 4 sccm, the distance between the magnetic sources to the TMT shower of 3 cm, the distance between the TMT shower to the substrate of 6 cm, and the bubbler pressure of 70 Torr were applied. A direct current of 165 A on electromagnet to satisfy the ECR condition of 875 G was supplied. We varied the microwave power values ranging from 800 W to 1100 W in order to observe its effects on the cell performances.

The STS316 bipolar plates were sliced into 1 cm^2 samples for the electrochemical tests. For a better surface roughness, the samples were sanded by the SiC abrasive papers of # 320, # 1000, # 2000 mesh and were polished with Al_2O_3 paste polisher of 5 μm and 1 μm using Mininet® 1000 (Buehler). The samples were then ultrasonically cleaned in the mixture solutions composed of 250 mL acetone, 100 mL water, and 150 mL methanol for 30 min. Fig. 1 depicts the reaction dependent on interactions between STS316 interface and FTO film determine relation with the plasma untreated and treated STS316. Before, the depositions were conducted, the polished samples were treated by H_2/Ar plasma for removing the impurities on the surfaces as described in Fig. 1.

To measure the sheet resistance of the BP surfaces, a four-point probe method was used, adapted from Smit et al. [12]. The electrical resistivity is determined based on the following Eq. (1),

$$\rho = k\frac{V}{I}t, \tag{1}$$

where ρ is electrical resistivity (Ω cm), k is correction factor, V is the measured voltage (V), I is the applied current (A), and t is the deposited film thickness (cm).

Fig. 2 shows the apparatus for the measurement of ICR of the STS316 coated FTO film. The tool utilized two pieces of conductive carbon papers sandwiched between the prepared specimen and two copper plates with the compaction force ranging from 50 to 300 N cm^{-2}. To obtain all electrochemistry properties of the specimen, the electrochemical measurements were carried out in the bubbled solution of 1 M H_2SO_4 + 2 ppm HF under nitrogen gas at 70 °C. The solution was prepared to simulate the fuel cell environment during its operation. The density of working electrodes was 7.810 g mL^{-1} with the equivalent weight of 27.5 g. The reference electrode type is SCE (stand calomel electrode) saturated calomel with the offset potential versus the normal hydrogen of 0.242 V. The result was then analyzed by the Tafel plot method in the optimized environment. A single cell was assembled from the FTO film coated SUS 316 bipolar plate and a commercially available membrane electrode assembly (MEA) covered by carbon papers compacted by a torque wrench with the force of 150 N cm^{-2}. The operated current density was 0.5 A cm^{-2} for the single cell measurement, while the 70% H_2 gas and the 40% air were employed as the fuel gases operated at the temperature of 343 K.

Total current density (i_t) was calculated from the cell voltage (V_{cell}) curve since no limiting current and internal current losses are received. The cell voltage for fuel cell is calculated from the Ref. [13], given by the Eq. (2):

$$V_{cell} = E_r - \frac{RT}{\alpha F}\ln\left(\frac{i_t}{i_0}\right) - i_t R_{i_t}, \tag{2}$$

where E_r is the reversible cell potential, given by the Eq. (3):

$$E_r = 1.482 - 0.000845\ T + 0.0000431\ T \ln P_{hydrogen}\sqrt{P_{oxygen}}, \tag{3}$$

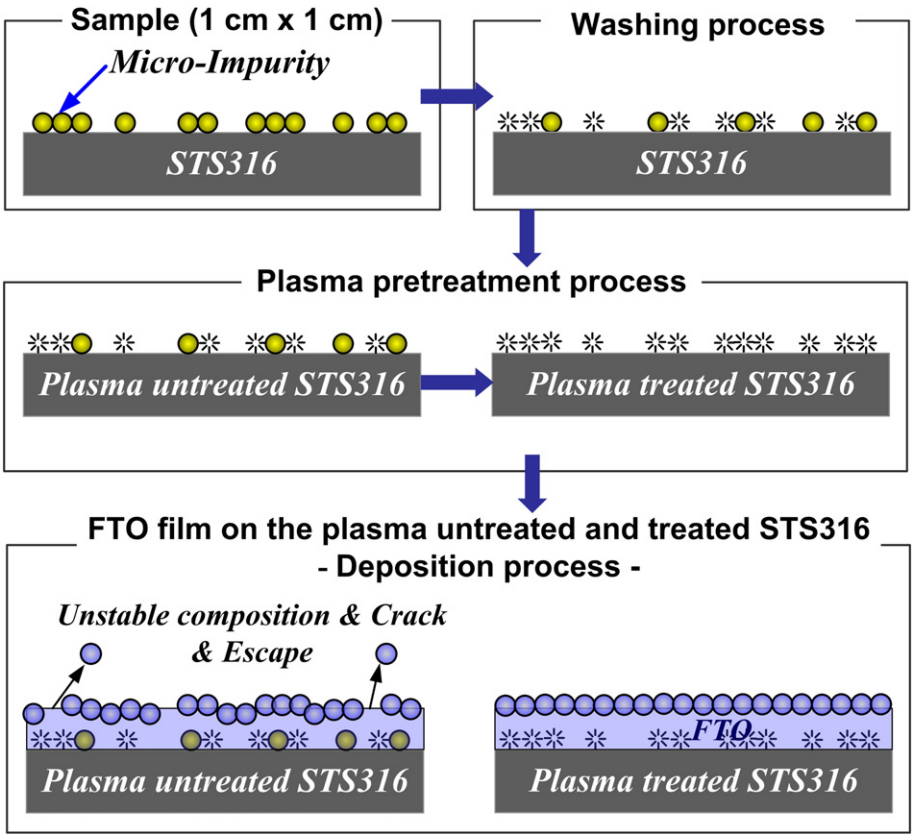

Fig. 1. Reactor dependent interactions between STS316 interface and FTO film determine the relation between the plasma untreated and treated STS316.