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Effect of manufacturing process sequence on the corrosion resistance characteristics of coated metallic bipolar plates

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HIGHLIGHTS

- Forming-coating sequence effects on the corrosion resistance of BPPs were examined.
- Two process sequence, forming methods, and PD-PS corrosion test methods were used.
- Corrosion performance of coating materials on BPPs was ZrN > CrN > TiN > uncoated.
- It was also found that thicker coating increased the corrosion resistance.
- Coating before manufacturing does not always decrease the corrosion resistance.

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ABSTRACT

Metallic bipolar plate (BPP) with high corrosion and low contact resistance, durability, strength, low cost, volume, and weight requirements is one of the critical parts of the PEMFC. This study is dedicated to understand the effect of the process sequence (manufacturing then coating vs. coating then manufacturing) on the corrosion resistance of coated metallic bipolar plates. To this goal, three different PVD coatings (titanium nitride (TiN), chromium nitride (CrN), zirconium nitride (ZrN)), with three thicknesses, (0.1, 0.5, 1 μm) were applied on BPPs made of 316L stainless steel alloy before and after two types of manufacturing (i.e., stamping or hydroforming). Corrosion test results indicated that ZrN coating exhibited the best corrosion protection while the performance of TiN coating was the lowest among the tested coatings and thicknesses. For most of the cases tested, in which coating was applied before manufacturing, occurrence of corrosion was found to be more profound than the case where coating was applied after manufacturing. Increasing the coating thickness was found to improve the corrosion resistance. It was also revealed that hydroformed BPPs performed slightly better than stamped BPPs in terms of the corrosion behavior.

1. Introduction

Metallic bipolar plates (BPPs) must be corrosion resistant since PEMFC environment is acidic and humid [1]. In order to improve the corrosion resistance of metallic BPP and meet the DOE (Department of Energy, USA) target for corrosion current density of lower than 1 μA cm^{-2} [2], surface treatments such as coatings are extremely important [1]. These coatings need to be electrically conductive and corrosion resistant. There are various coating material alternatives such as polymers, noble metals, metal nitrides, metal carbides, etc. that can be applied on metallic plates to satisfy the DOE target [3]. Carbon based or metal-based coating materials are widely reported in literature [4]. Studies available in the literature mostly preferred the physical vapor deposition (PVD) method for coating of metallic materials against corrosion [5–7].

Garcia and Smit selected the polypyrrole coated SS 304 sheet sample to study the corrosion endurance of the coating. The electrodeposition method was employed to cover a 1 cm^2 surface area of the substrate material with diverse amount of polypyrrole. They observed that polypyrrole improved the corrosion behavior of the sample, however; determining the optimum coating composition was required to achieve long-term stability in PEMFC [8]. Wang and Northwood also examined the effect of polypyrrole coating material on the corrosion behavior of SS 316L. Galvanostatic and cyclic

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voltammetric processes were used to deposit the coating on the 2.25 cm^2 surface area [9]. It was concluded that the positive effects of polypyrrole coating on corrosion resistance was similar to that in Garcia and Smit. Ren and Zeng combined the polypyrrole with a polyaniline to have a bilayer composite coating material in their study. They reported that composite coating was better than single polypyrrole coating in terms of the corrosion characteristic [10]. Joseph et al. tested two polymer-coating materials (polypyrrole, polyaniline) in their work. They supported the previous results by others regarding with the good corrosion behaviors of these coatings [11]. Morks et al. reported promising corrosion resistance results for plasma-sprayed W-Ni coatings [12]. Another work by Lee and Lim investigated a polymer composite of polyamide-imide filled with carbon black by determining the optimum carbon black content for BPP's better corrosion and lower contact resistance [13].

Lee et al. compared the corrosion resistance SS 316L and AA 5052 sheets that were shaped into the BPPs via CNC machining or EDM. The AA 5052 sheet was coated with the YZU001 diamond-like coating by means of physical vapor deposition (PVD) technique while the SS 316L used as uncoated. Although the SS 316L was uncoated, it demonstrated higher corrosion resistance than the coated AA 5052. Nevertheless, the aluminum possessed lower contact resistance value compared to SS 316L sheet [14].

Similar to many other researchers, Yu et al. selected the SS 316L material to test the coating influence on corrosion behavior. Authors coated the SS 316L sample with a tantalum (Ta) coating through PVD process. Comparison between uncoated and coated SS 316L samples disclosed that the Ta coating improved the corrosion resistance of the sample [6].

Jung et al. manufactured the BPPs from the titanium block with the dimension of 7.5 × 7.5 × 1.2 cm. The BPP had serpentine type flow-fields with 1 mm-deep channels, and 5 cm^2 surface area. The BPP, covered with 1 μm gold coating, increased the unit cell performance by blocking the oxidation forming on surface [15]. Similarly, Kumar et al. noted that gold coatings provide excellent corrosion protection for metallic BPPs even with nanometer thickness level (10 nm) [1]. In another study by Yun, firstly the 0.1 μm titanium or nickel, and then the 1 μm and 2 μm gold was deposited on the surface of SS 316L blanks by electron-beam-evaporation process. Results indicated the gold-coated samples as appropriate BPP candidates in PEMFC [16].

Yoon et al. studied several substrates (SS 304, SS 310, SS 316) and coating materials (Ti, Zr, ZrN, ZrNb, ZrNAu, 2 nm–10 nm–1 μm-thick gold) through PVD coating process. Both anode and cathode environments of PEMFC were simulated in polarization tests for coated metal samples with a 3 cm^2 surface area. According to the corrosion test results, Zr, ZrN, ZrNb, ZrNAu and 10 nm-thick gold-coated samples met the DOE target in the anode side while only the Zr coated sample reached the DOE target in the cathode side. Moreover, thicker coating materials were found to demonstrate higher corrosion-resistance [17]. Barranco et al. reported the corrosion behaviors of single chromium nitride (CrN) and multilayer zirconium-chromium nitride coatings on the AA 5083 alloy. Coatings were applied by means of the cathodic arc evaporation physical vapor deposition (CAE-PVD) method on one side of the samples. Short-term corrosion tests confirmed the suitability of these coatings and the PVD coating method for aluminum plates [7].

Jeong et al. and Feng et al. experimented on Ni–Cr rich-coating-layers and reported that the amount of Ni–Cr content should be optimized to accomplish expected corrosion resistance for SS 316L BPP in PEMFC [18,19]. Barronco et al. investigated the BPPs of CrN-coated AA 5083 by using three different coating thicknesses (3, 4, 5 μm). Although CrN coated AA 5083 displayed better corrosion resistance compared to uncoated aluminum, it may not be appropriate for BPP since some corrosion pitting holes were detected on the surface after corrosion test [20]. On the other hand, Tian and Fu et al. also researched CrN film on the SS 316L BPP material and their results noted promising features of CrN in terms of electrochemical stability and interfacial electrical conductivity [21–23].

Wang et al. utilized TiN coating on the SS 316L with the PVD coating technique. Two electrochemical (potentiodynamic and impedance) test methods were used to evaluate the corrosion resistance. Approximately 15 μm-thick TiN coating was found not to be a good coating option for BPP since it incorporated pinholes [24]. Zhang et al. preferred SS 304 substrate material as BPP to observe the corrosion-resistance performance of TiN coating. Different from Wang et al., Zhang et al. implemented two different coating processes: pulsed bias arc ion plating (PBAIP) and magnetron sputtering (MS) in their study. The results specified Ti_2N/TiN multilayer coating as the corrosion resistant coating for BPP [25].

Eriksson at al. studied the formability and corrosion behavior of TiN-coated AISI 304 stainless steel. Corrosion tests were conducted after the forming process. The authors reached following conclusions;

1 Hard coating did not prevent the formability of the coated sheet,
2 Although some cracks were observed under the microscope after the manufacturing process, uniform coating color was still seen on the surface,
3 With higher coating thicknesses, cracks numbers declined,
4 Forming process reduced the corrosion resistance of TiN coated sample, however, TiN coated sample showed better corrosion protection than the uncoated sample as expected [26].

There are several other studies on performance of TiN, CrN, TiAlN, CrN–Ti, TiC and multilayer TiN/CrN coatings applied mostly on SS 316L substrates [27–35].

Fu et al. studied three different carbon-based films (C, C–Cr, and C–Cr–N films) as coating materials for SS 316L BPP. Only the C–Cr film coated sample was found to be suitable in PEMFC conditions according to potentiodynamic and potentiostatic test results [36]. Feng et al. also coated SS 316L coupons with carbon film. Amorphous-carbon (a-C) coating was processed via close field unbalanced magnetron sputter ion plating (CFUBMSIP) technique. They concluded that a-C could be an alternative coating material for the metallic BPPs [37]. The positive effects of the carbon-based coatings on the metallic BPP in corrosion resistance were repeated by Fukutsuka et al. and Lee et al. [38,39].

Another way to improve corrosion resistance and lower the contact resistance of BPP is surface modification methods [40]. Lee et al. applied surface treatment on the SS 316L specimen to obtain a better surface quality resulting in high corrosion resistance and low contact resistance. They observed that since the surface became smoother after treatment, the sample was developed into a more corrosion resistant material [41]. Cho et al. performed the chromizing surface modification on SS 316L material by pack cementation method. This treatment improved the corrosion protection feature of the sample in short-term tests, while no development on the corrosion behavior was seen after 10 h-long-term test [42]. In addition, chromized steels were recommended in terms of the electrochemical stability in literature [43–46]. Another option to coat BPP is niobium, which was reported in literature with promising anti-corrosion performance [47–49].

All of these studies showed that corrosion resistance target can be satisfied, however; in most of them, both corrosion and contact resistance targets were not satisfied at the same time. The contact resistance target level set by DOE is less than 10 mΩ m^2 at