A Review of Metallic Bipolar Plates in Proton Exchange Membrane Fuel Cell

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Abstract

proton exchange membrane (PEM) fuel cells are of prime interest in transportation applications due to their relatively The high efficiency and low pollutant emissions. Bipolar plates are the key components of these devices as they account for significant fractions of their weight and cost. According to the materials that used in their manufacturing, the bipolar plates categorize to: metallic, composite and graphite plates. One of the disadvantages of composite and graphite plates is the higher weight and volume of cell's stack because of small deformation ability and weak stampability property of these plates. So the industrial use of metallic plates is usual. The disadvantages of metallic plates are Low corrosion resistance in acidic environment, increasing of the interfacial contact resistance caused by presenting of the oxide layers on the surface of metallic plates and creating of ionic contamination caused by corrosion products. Therefore bipolar plates with a conductive coating and are resistant to corrosion covered. This paper offers a comprehensive review of the researches on the metallic Bipolar plates, covering materials and fabrication methods   .

Key words: metallic bipolar plate, composite bipolar plate, proton exchange membrane fuel cell ,corrosion resistance.

Introduction

The global climate changes produced by greenhouse gases emissions such as CO_2 ,NO_x and SO_x

that are ongoing throughout the world pose a progressively higher demand for replacing today's fossil fuel based energy production by less pollutant technologies [1, 2]. Among the alternative energies available proton exchange membrane (PEM) fuel cells have been considered to power transportation vehicles such as automobiles and buses due to their high power density, relatively quick start-up, low operating temperatures and low greenhouse gas emissions .[3]

Nevertheless, to completely achieve the automotive industry requirements PEM fuel cells have to overcome some intrinsic limitations mainly related to durability and cost compared to conventional internal combustion engines [4]. The main components of a PEM fuel cell structure are bipolar plates and the membrane electrode assembly (MEA). The MEA comprises the proton exchange membrane, gas diffusion layer (GDL) and a catalyst layer. A schematic view of such structure is shown in Figure 1 In a fuel cell stack the bipolar plates are key elements as they account for large fractions of the total weight, volume and cost of the stack. According to Tsuchyia and Kobayashi [5] bipolar plates may reach up to 80% of the total
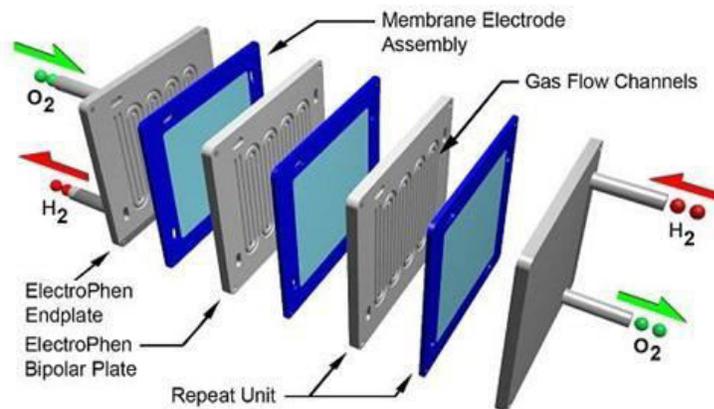
Components of hydrogen fuel cell. Figure.1

weight and 45% of the total cost in a PEM fuel cell stack. More recent data show that the relative cost has fallen to about 25% of the stack [6], yet a very significant amount. Furthermore these components play vital functions in the stack such as to carry electric current away from each cell, to distribute fuel and oxidant homogeneously within individual cells, to separate individual cells and to facilitate the water management within the cell [7]. To perform such a number of

functions a variety of materials have been proposed to the manufacturing of bipolar plates. The main properties that any material must present to be used in these devices are well established by the United States Department of Energy (DOE). The earlier traditional option was the use of non- porous graphite plates due to their intrinsic high electrical conductivity and chemical stability in the PEM fuel cell aggressive environment. Although the performance of graphite plates are suitable related to these properties they are brittle and lack mechanical resistance. Another drawback is the need for machining the flow field channels which raises the manufacturing cost making it prohibitive for mass production [8]. Alternatives to pure graphite plates are composite bipolar plates based on the mixture of polymers and graphite particles. This class of materials allows mass production at a reasonable cost using manufacturing processes such as injection molding for thermoplastics or BMC for thermosets. There are several examples of graphite-based composite bipolar plates using polypropylene (PP), polyphenylene sulfide (PPS), phenolic and vinyl ester resins as matrices [9–13]. The polymer matrix gives flexibility to the bipolar plate improving its mechanical strength. The chemical stability is also not badly affected by the since polymers are insulating materials. Thus it is mandatory to formulate a composite bipolar plate with careful to attain mechanical performance without sacrifice electrical conductivity.

In spite of all the advantages of graphite-based composite bipolar plates regarding to their low weight, high production and chemical stability, if one compares their overall performance with that of metal bipolar plates two major drawbacks become evident, that is, their lower mechanical resistance and electrical conductivity. Considering especially transportation applications metal bipolar plates are more resistant to mechanical shocks and vibrations that could lead to Cracking and leaking of reactant gases. Cunningham [14] presented Data showing that the electrical conductivity of metal bipolar plates may reach up to 1000 times that of composite ones. In addition, they present easy manufacturability at low cost which increases their competitiveness in the fuel cell market [15]. However, a significant handicap that may decrease metal bipolar plates' performance is the susceptibility to corrosion in the acid and humid environment of PEM fuel cells. Metals operating in the fuel cell with a pH of 2–4 and temperatures around 80 ^{o}C may suffer dissolution. The ions leached may poison the membrane electrode assembly (MEA), decreasing the power output of the fuel cell [16,17].   Furthermore,

passive layers formed during operation increase the electrical resistivity of metal bipolar plates. Consequently, the fuel cell efficiency is also negatively affected due to the raising of interfacial contact resistance as the oxide layer grows. These effects offset the advantage of high electrical conductivity [18]. The problems outlined above may be overcome or minimized by protecting metal bipolar plates from the corrosive fuel cell operating conditions with coatings [19]. A wide variety of alternatives have been proposed in research works towards this objective. This paper aims to present major research topics and results in the corrosion protection and characterization of metal bipolar plates for PEM fuel cells. Different coating methods and substrate materials are addressed giving a comprehensive overview on this subject .

Non-coated metals

Nobel metals such as gold and platinum have low Interfacial contact resistance (ICR) and high corrosion resistance, therefore their fuel cell performance when used as a bipolar plate perform very similar to Poco graphite bipolar plates [20, 21]. In some cases, they showed better performance than Poco graphite. However, the high cost of these metals has prohibited their utilization for commercial use .

Major concerns have focused on metal corrosion and a decrease in ICR values once surface passivation film forms. Candidates such as stainless steel have been tested and used as bipolar plates. For example, Hermann et al. [8] reported that aluminum, stainless steel, titanium and nickel bipolar plates exposed to an operating environment similar to that of a fuel cell (pH: 2-3; T ~ 80 $^{\circ}$C) were prone to corrosion or dissolution. A corrosion layer on the surface of a bipolar plate increases electrical resistance and decreases cell output. While this surface oxide layer protects the metal and stops the corrosion from progressing to the lower layers, it forms an electrically insulating interfacial layer. As the thickness of the oxide layer increases, ICR also increases that accordingly causes a decrease in electric power output. Davies et al. [22] observed that under compaction pressure of 220 N/cm^{-2} imposed in fuel cell experiments, the relative ICR of various grades of stainless steel decreased in the order 321 > 304 > 347 > 316 > Ti > 310 > 904 > Incoloy 800 > Inconel 601 > Poco graphite. For high alloy materials, the same authors observed that the oxygen was not as prominent as it was in other grades of stainless steel, which suggested that the passive film was thinner in these samples. The results showed that the passive

film decreased in thickness according to the order 321 > 304 > 316 > 347 > 310 > 904 > Incoloy 800 > Inconel 601. Poco graphite, with the lowest surface resistive losses, produced the highest potentials, with increased polarization observed for metal plates in the order of Poco graphite < 310 < Ti < 316. The data indicated that the performance of the bipolar plates is related to thickness of the passive layer and ICR: as the thickness and ICR increase, more heat energy is generated and less output electric energy is produced. Wang et al. [16, 23] found that both austenitic (349TM) and ferritic (AISI446) stainless steel with high Cr content showed good corrosion resistance and could be suitable for bipolar plate application, though AISI446 requires some improvement in ICR due to formation of a surface passive layer of Cr_2O_3 .The same authors also verified that Cr in the alloy formed passive film on the surface of stainless steel. As the Cr content in stainless steel increased, the corrosion-resistance improved as it is commonly known in the corrosion field and the results agreed with the findings of Davies et al. [22]. However, a thick non-conductive surface passive layer of Cr_2O_3 will produce an undesirable high ICR. Wang and Turner [23] studied stainless steel samples of AISI434, AISI436, AISI441, AISI444, and AISI446. They noted that in both PEM fuel cell anode and cathode environments, AISI446 steel underwent passivation and the formed passive films were very stable. An increase in ICR between steel and carbon backing material due to passive film formation was also reported. The same authors indicated that the thickness of passive film on AISI446 was estimated to be 2.6 nm for the film formed at 0.1V in the simulated PEM fuel cell anodic environment and 3.0 nm for the film formed at 0.6V in the simulated PEM fuel cell cathodic environment. The authors recommended that further improvement in the ICR would require some modification of the passive film, which was dominated by chromium oxide. They also stated that ICR for AISI446 increased after passivation. The XPS depth profiles indicated that air-formed surface film composed of iron oxides and chromium oxide but neither dominated. The passive films on AISI446 were mainly chromium oxide, and the iron oxides played only a minor role. In simulations of the PEMFC, the passive film formed on the cathode was thicker than that formed on the anode, with the former resulting in higher ICR. Metals such as Al, Ti, Ni, etc. similarly form a surface passive layer, in fuel cell acidic environment, which has good corrosion resistance but poor ICR. Moreover, for uncoated metals, ions and oxides could directly foul the solid electrolyte and tarnish the catalyst in the MEA that result in considerable adverse

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effects on the cell performance. Specifically, as unprotected metal bipolar plates are exposed to a corrosive environment inside a fuel cell in which, relative humidity (> 90%), acidity (pH = 2-3) and temperature (60-80 ^{o}C), metal dissolution will occur. The dissolved metal ions diffuse into the membrane and then get trapped in the ion exchange sites inside the ionomer, resulting in lowered ionic conductivity as described by Mehta and Cooper [24]. A highly conductive corrosion resistance coating with high bonding strength at the interfacial layer between base metal substrate and coating layer is required to minimize this problem.

3Coated metals

Metallic bipolar plates are often coated with protective coating layers to avoid corrosion. Coatings should be conductive and adhere to the base metal without exposing the substrate to corrosive media [25]. Noble metals, metal nitrides and metal carbides are some of the metal-based coatings that have been explored [21,26-29]. To be effective, the coefficient of thermal expansion of base metal and coating should be as close as possible to eliminate formation of micropores and microcracks in coatings due to unequal thermal expansion [26]. In addition, some coating processes are prone to pinhole defects and viable techniques for coating bipolar plates are still under development [8]. Mehta and Cooper [24] presented an overview of carbon-based and metallic bipolar plate coating materials.. Woodman et al. [26] concluded that the coefficient of thermal expansion (CTE), corrosion resistance of coating, and micro-pores and micro-cracks play a vital role in protecting bipolar plates from the hostile PEM fuel cell environment. The authors also argued that even though PEM fuel cells typically operate at temperatures less than 100 ^{o}C, vehicle service would impose frequent start up and shut down conditions, and temperature differentials of 75-125 ^{o}C would be expected during typical driving conditions. A large difference in the CTE of the substrate and coating materials may lead to coating layer failure. One technique to minimize the CTE differential is to add intermediate coating layers with less CTE mismatch between that of adjacent layers. Materials such as Al, Cu, Sn, Ni and Ni phosphorous are very susceptible to electrochemical corrosion in acidic solutions that are typical of PEMFC operating conditions. However, gold shows very high resistance to electrochemical corrosion, comparable to graphite, the traditional bipolar plate material. Table1

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lists the substrates, coatings, and measured properties (ICRs and corrosion resistivities) of several metallic BPs reported in the literature .

.3.1Metallic coatings

Metallic coatings include Coatings such as nickel, Nickel - phosphorus coating is the noble metals such as gold and platinum   .

.3.1.1Noble-metal-coatings

Other compounds that are suitable to be coated on SSs in order to provide a conductive and protective layer are noble metals such as gold, silver, and platinum. Silver is well known for its excellent electrical conductivity, high corrosion resistance, and relatively low cost. Feng et al. [30] used ion implantation technique for coating a thin layer silver on SS 316L. The potentiostatic tests revealed a significant decrease in I_{Corr} from 10 to 0.7 µAcm^{-2} after Ag implantation. In addition, the test showed that ICR value improved from 312 to 78 mΩcm^2 .The results showed that the overall reduction in ICR by ion implantation depends on the value of precipitated silver nanoparticles in the implanted layer, the passive layer thickness, and amounts of metallic phase of silver and nickel. In addition, the coating method, coating process conditions (especially temperature), surface pretreatment, and the coating thickness can obviously affect the coating quality, thereby ICR value   .

Hentall et al. [20] machined current collectors from Al to the exact dimensions of graphite bipolar plates, then coated it with Au by a solution process. The plates were then used in a fuel cell and during initial warm-up, the data indicated performance very similar to graphite (1.2 A/cm^2 at 0.5 V) because an Au coated Al plate had a similar ICR with gas diffusion media (GDM) to graphite. However, the performance degraded quickly to 60 mA/cm^2 at 0.5 V. The analysis revealed that some of the Au coating lifted from the plate and physically embedded in the membrane. Wind et al. [21] also indicated that Au-coated bipolar plate (SS316L) clearly demonstrated no difference between the metal-based and graphite plates due to the same reason mentioned above

Substrate	Coating	Method	$I_{Corr.}$ (µAcm^{-2}(	ICR (mΩcm²(	Ref.
					Bare Metallic Plates
SS434, SS436, SS441, SS444, SS446	-	-	SS446 (10-15), SS444(50), SS436(60), SS434 (200), SS 441 (300)	before operation SS446> SS434> SS441> SS436> SS444 (between 100-200); After passivation SS446(280 in anode and 350 in cathode(	[23]
SS 321, SS 304, SS 347, SS 316, Ti, SS 310, SS904L, Incoloy800, Inconel601, Poco Graphite	-	-	-	before operation 321SS(100), 304SS(51), 347SS(53),316SS(37), Ti(32), 310SS(26), 904SS(24), Incoloy800(23), Inconel 601(15), Poco Graphite(10); After1200h operation Ti(250), SS316(44), SS310(28), Poco Graphite (10)	[22]
Fe- and Ni-based amorphous alloys: Fe-Al2, Fe-Al1N1, Ni-Ta5	-	-	anode potential at -0.1V at 80C, 1M H2SO4+2ppmF- with hydrogen bubbling, FeAl2(140), Fe-Al1N1(48), Ni-Ta(52)5	before operation-8) , (20	[31]
SS316L, SS321,			SS316L , SS321, SS347, Inconel		

	SS347, Inconel625, Incoloy825, HastelloyC-276, Tantalum, Ti		-	-		625, Incoloy825,HastelloyC-276, Tantalum, and Ti are 26, 8, 15.8,4, 6.4, 4.8, 0.0126, and 1260, respectively at120°C; 316L, 321, 347, Inconel625, Incoloy825, and HastelloyC-276 are 12.6, 2, 5, 0.11, 4, and 0.8, respectively, at 80°C	-	[32]
					Coated metallic plates			
	SS 316 L		Cr-nitride	-		SS 316 (~300), Cr-Nitrided SS(1) 316	bare SS 316 (55); Cr-Nitrided SS 316 (10)	[33]
	SS304		TiN and Ti_2N/TiN	Pulsed-arc ion plating and magnetron sputtering		SS304(2.6), SS304/TiN (0.145)	SS304(~140), SS316/TiN(19) at 240 Ncm^{2-}	[34]
	SS316L		CrN	PVD		in anodic condition (0.5); in cathodic condition(1.3)	30	[35]
	SS 316L		CrN, Cr_2N	ICP-PVD		,(4.3>)coating at 590 K in cathodic condition	bare SS316L (80); CrN40, 13, and 11, respectively-coating in 530, 590, and 650K are	[36]
	SS316L		Cr/CrN/Cr	Arc ion plating		1.00–0.56	35	[37]
	SS 316L		CrN	ICP		bare SS316L (4.76), CrN-	82.2	[38]

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						coated SS316L (0.157), Cr-plated SS316L(25.5)	
	SS316L		Amorphous carbon	Sputter ion deposition		bare SS316L (0.06), In anodic condition C-SS316L (43.1); In cathodic condition C-SS316L(21)	bare SS316L(477-255.4), C-SS316L (8.3–5.2), Graphite (10.4–5.4), between 120–210 Ncm^{2-}	[39]
	SS 316L		CrN/TiN	RF-sputtering		in the ratio of CrN/TiN at 1:9, 3:7, and 5:5 are (0.76), (0.82), and(1.45)	0.88in bare SS and ≈84 in coated SS	[40]
	SS316L		silver nano particles	Ion implantation		bare 316L(10), nanolayer silver coated SS(0.7)	bare SS(312), nanolayer silver coated(78)	[30]
	SS316L SS304 Ni-alloy 3127 Ni-alloy 6020 Ni-alloy 5923		CrN coated on SS	PVD		in cathodic condition SS304 (3.26), SS316L (1.92), SS304/CrN(0.24), SS316/CrN (0.79), Ni3127 (3.14), Ni6020 (4.97), Ni(1.95) 5923	Graphite (3.5), Ni-based alloys(≈3.8), SS304 (95), SS304/CrN (19), SS316L(90), SS316L/CrN (12); at 220 Ncm^{2-}	[41]
	Ni-50Cr alloy, 349TM SS		5-3µm Nitriding	Thermal nitridation		In Anodic condition Nitrided Ni-50 Cr(3-4), Nitrided 349 TM(15-20); In cathodic condition 349TM(0.25~)	bare Ni-50CrL(~60), nitrided Ni-50Cr(~10), SS349(~100), Nitrided-SS 49 (10~)	[42]
	Hastelloy G-30, G-35), SS(AL29-4C(		Nitriding	Thermal nitridation		in anodic condition, Nitrided G-35 (0.5), Nitrided AL29-4C(0.3)	bare G-30 & G-35 (between 30-75), AL29-4C (>100); Nitrided G-30 & G-35 (≈10), Nitrided AL29-4C (10<)	[43]
	Ti		Nitriding	Plasma-ion implanta		bare Ti (1.45), high-temperature-	bare Ti (1.82), high-temperature-	[44]

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			tion		Nitrided Ti (0.22), low-temperature-Nitrided Ti (0.86)	Nitrided Ti (12), lowtemperature-Nitrided Ti (440)	

Table1 lists the substrates, coatings, and measured properties ICRs and corrosion resistivities of metallic BPs.

.3.1.2 Ni-P electroless plating

One of the appropriate techniques for coating the layers on the BPs is an electroless plating method. In order to increase corrosion resistivity, Ni-P coating on stainless steels is commonly utilized in industry. Although, this coating method is very simple and just needs a homogenous solution bath at constant temperature and pH, this method does not seem cost effective due to using the expensive organic materials [45]. It should be emphasized that the thickness uniformity of coating for electroless method is more than that of other methods such as electroplating Lin et al. [46], employed electroless plating method to cover a Ni–P layer upon SS316L. The potentiostatic test for the Ni–P deposits prepared under the optimal condition was performed in a simulated anode working environment (0.5 M H_2SO_4 10 + vol% methanol). The test results showed a negative corrosion current at all times indicating the cathodic protection of SS during the test. Even after 10 h potentiostatic treatment, no metal ions were found in the test solution. In addition, the result of a performance test demonstrated that stainless steel BPs coated by Ni–P layer obtained a lower bulk resistance and an enhanced cell performance in comparison with commercially available plates. The Ni-P coating on SS316L by using Cu-interlayer demonstrated a higher output current compared to the commercial PEM fuel cell, with ~18% growth in performance, but I_{Corr} is higher than DOE criteria. Fetohi et al. [47] studied on coating of Ni-P and Ni-Co-P on Aluminium alloy 5251 by electroless and electroplating methods. I_{Corr} of Ni-Co-P coated plate was improved by four times with respect of that at the bare AA5251 substrate. The least I_{Corr} by electroless and electroplating methods were related to Ni-Co-P ($3.21 \times 10^{5-}$Acm^{-2} (and Ni-P ($1.13 \times 10^{7-}$Acm^{-2} ,(respectively. The electroless method resulted in an ICR value as high as 114 mΩcm^2 that is twice the amount of that for coating by electroplating (54 mΩcm^2 .(The results of this research showed that Ni-P coatings are not suitable for usage in BPs   .

.3.2 Conducting polymer based coatings

Shine et al. [48] electrochemically coated 304 stainless steel with conducting polymers polyaniline (PANI) and polypyrrole (PPY). Cyclic voltametry was used for polymerization and deposition of these polymers. The polymer-coated stainless steel plates were tested for corrosion and ICR under PEM fuel cell conditions. An improved corrosion resistance with acceptable ICR was observed but cost, durability, and volume production were not mentioned in the study   .

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.3.3 Composite coatings

One of the paths to decrease corrosion rate of metallic BPs is the coating of metals by a thin polymerbased composite layer. Lee et al. [49] developed an Al-based BP coated with a thin layer of polypropylene/carbon black composite. They used carbon paper and CB as interlayer to decrease ICR between composite and Al layer. They reported the ICR value lower than 21 $m\Omega cm^2$ and I_{Corr} lower than1 μAcm^{-2} after a long time. However, the bond strength between layer and substrate is doubtful. On the other hand, the high thickness of composite BPs increases volume and weight of the stack. Mawdsley et al. [50] also coated polymer-based composite on Al by wet spraying followed by heat treatment. The composite contains ethylene tetrafluoroethylene as polymer and TiC and graphite poweders as fillers. In-plane electrical conductivity, cathodic corrosion resistance, flexural strength, and flexibility tests related to the aluminum plate showed that the composite coated aluminum plates met the DOE targets for BPs .

.3.4 Carbon-containing coatings

 The carbon films also seem to be suitable coatings on SS. Feng et al. [51], deposited an amorphous carbon film on SS316L by close field unbalanced magnetron sputtering. The results obtained from the potentiodynamic, potentiostatic, ICP, and SEM analyses consistently demonstrated that the corrosion resistance was significantly improved by the carbon film. In particular, the current densities under the cathode operation, potential were reduced from 11.26 μAcm^{-2} to 1.85 μAcm^{-2} .Tests showed that the carbon film is stable and greatly reduces the corrosion rate of the SS316L.

In addition, the contact angle of water droplet on the uncoated SS316L was much smaller than that of the carbon coated one suggesting that the carbon coated SS is more hydrophobic. This property substantially eases eliminating the water droplets produced in cathode side, thereby inhibiting water flooding in fuel cell stack. The results of the ICR test showed that ICR of carbon coated SS316L changes from 10.2 to 5.2 $m\Omega cm^2$,by increasing clamping pressure from 90 to 210 Ncm^{-2} ,that is much lower than ICR with bare SS316L (380 $m\Omega cm^2$.)

The high ICR of bare SS is related to the formation of the chromium oxide layer naturally coated the SS surface in the atmospheric environment. This research demonstrated that carbon coated SS316L BPs could reduce the volume and cost of PEM fuel cells and increase their performance and durability. However, the final assessment upon carbon coated SS strongly depends on the results of long time fuel cell tests that there are few reports on this case. It has been reported that the carbon film coating on SS is facilitated by Ni interlayer [52]. Chung et al. [52] coated nickel layer to catalyze the carbon deposition upon SS304 plate. Afterwards, a thin layer of carbon was covered with substrate (at 680 $^\circ$C under C_2H_2/H_2 .[53] (Analyses indicated that the carbon film displays double layer structures, i.e. the highly ordered graphite layer at the carbon/Ni interfaceand the surface layer mainly containing disarranged graphite structures .

        It was specified that the surface morphologies of carbon deposits remarkably depend on the concentration of carbonaceous gas. Both corrosion endurance tests and PEM fuel cell operations showed that the carbon film revealed excellent chemical stability similar to high-

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purity graphite plate, which successfully protected SS304 substrates against the corrosive environment in PEM fuel cell. Therefore, it can be predicted SS/Ni/carbon plates may practically be used instead of the commercial graphite plates in the application of PEM fuel cell.

In another work, a series of Cr-containing carbon films were deposited on SS316L substrates as BPs for PEM fuel cell [54]. Doping Cr in carbon film would considerably influence the sp^3 and sp^2 carbon atom content (the higher content of sp^3/sp^2 ratio of carbon atoms, the higher ICR value). With the aid of the surface Cr-containing carbon film, ICR and corrosion resistance of the SS316L substrate are greatly improved. The SS316L substrate coated with $Cr_{0.23}C_{0.77}$ film exhibited the lowest ICR (2.8 $m\Omega cm^2$ (and the highest corrosion resistance ($9.1\times10^{-2}\mu Acm^{-2}$ (in simulated corrosive conditions of PEM fuel cell. The above researches indicate that the carbon-bearing films can be a suitable alternative coating for stainless steels to be used for metallic Bps .

.3.5 Diamond like coating

Lee et al. [55] applied PVD coating of YZU001 like-diamond film on the 5052 Al alloy and SS316L and compared their performance to that of graphite. The corrosion rates were determined by Tafel-extrapolation method from the polarization curves. The coated Al, 316L stainless steel and graphite were fabricated into a single cell to measure ICR and to test cell performance. The metallic bipolar plates, PVD coated 5052 aluminum and SS 316L, performed better than the graphite material at low voltage but experienced shorter cell life. It was also observed that the SS316L plate with its naturally formed passive film had better corrosion rate than the YZU001 coated Al plate. The ICR of stainless steel was higher thus reducing its single cell performance. The coated Al plates had better ICR and single cell performance; however, the cell life was shorter .

.3.6 Nitrogen-containing coatings

Chromium nitride (CrN) is one of the suitable and famous coating layers to be coated on stainless steels, because it considerably decreases the I_{Corr} and ICR [42, 43]. Park et al. [56] have studied on the effects of a CrN/Cr coating layer on the durability of SS430 metal BPs under a fuel recirculationsystem of DMFCs. It was revealed that the CrN/Cr coating layer decreased ICR from 2000 $m\Omega cm^2$) for bare SS430) to 4 $m\Omega cm^2$) for CrN/Cr coated SS430). I_{Corr} was about 10-5 μAcm^{-2} in bare SS430 and 10-7-10-6 μAcm^{-2} in coated one. Brady et al. [43, 57] attempted to obtain low ICR and high corrosion resistance by nitridation of Cr-bearing alloys, such as Ni-Cr alloys and ferritic high-Cr stainless steels. CVD and PVD are two economically favorable methods for making protective layers on stainless steel .

Surface modification by thermal nitridation is one of the solutions for decreasing I_{Corr} and ICR of BPs to form a mixed nitride/Cr-nitride/oxide structure on the surface of the stainless steel [42, 43]. However, high temperature thermal nitridation (about 900°C) produces non-continuous and discrete external Cr-nitrides, thereby creating Cr-depleted regions and decreasing corrosion resistance [58, 59]. On the other hand, nitridation in high temperature leads to creating the precipitates such as CrN, Cr_2N and TiN, as well as Cr depleted regions that is more conductive than passive film (chromium oxide) [60-62]. It means that the nitridation in very high temperature would decrease ICR. Consequently, nitridation in high temperature is associated chiefly with the fact that the formation of Cr-nitrides leads to a loss of Cr from the matrix,

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thereby reducing the corrosion resistance of stainless steels [58, 36]. However, un-continuous and discrete Cr nitrides resulted from the nitridation at high temperature, would have a positive effect on decreasing ICR, because inhibits the creating the continuous passive film (chromium oxide phases). On the other hand, decreasing nitridation process temperature may severely decrease atomic diffusion, decrease the coating thickness, and produce insufficient value of the precipitates such as CrN, Cr_2N and TiN. These can lead to increasing corrosion current density and ICR. Therefore, it is anticipated that the temperature of nitridation should be optimized. There are few researches upon optimizing the nitridation temperature, but some of these researches verify the mentioned statements. Below, some of these researches are investigated. The results of research of Lee et al. [59] almost verify the mentioned claims. They performed thermal nitridation in two temperatures (at 700 °C and 900 °C) on 446M stainless steel. They found that after nitridation, ICR of stainless steel significantly decreased. They explained that nitridation leads to the formation and exposure of Cr nitrides, such as the CrN, on the surface of stainless steel and these precipitates help reduce the contact electrical resistance. In addition, the polarization curves revealed that the coated steel at 700 °C has excellent corrosion properties under PEMFC operating conditions, whereas the coated steel at 900 °C has relatively poor properties. They explained that the low-temperature nitridation of stainless steel produces a protective CrN/Cr_2O_3 layer, which protects the base metal from corrosive attacks. It was specified that ICR value, I_{Corr} in simulated anode condition, and I_{Corr} in simulated cathode condition for nitrided SS446M at low temperature is 6 $m\Omega cm^2$ $^{6-}10 \times 1$,Acm^{-2} ,and 1×10 $^{7-}Acm^{-2}$,respectively, which are much lower than that of the bare SS446M   .

Tian et al. [63, 64] reported that ICR could be reduced to 10 $m\Omega cm^2$ by plasma nitriding (at 370 °C for 2 h) of SS316L as well as SS304L, However I_{Corr} was more than 10 μAcm^{-2} that is not acceptable. They anticipated that conducting the coating process at high temperature (370°C) could lead precipitating more CrN precipitates, thereby more extensive chromium depletion and lower corrosion resistivity. In an attempt, Hong et al. [36] tried to optimize the temperature of nitriding process of SS316L. They performed the coating process at different temperatures 257, 317, and 377°C by using inductively coupled plasma. It was revealed the least value of ICR was achieved at 317°C (13 $m\Omega cm^2$,(whereas, the least value of corrosion current density was achieved at 257°C ($3.43\times 10-6$ Acm^{-2} at 0.6 V). These results verify this claim that the temperature of coating process should be optimized to decrease either ICR or corrosion current density.

It was revealed that using high-density plasma nitiriding could reduce the process temperature, so that Cr depletion was not significant In another study, Yang et al. [65] clearly stated the advantages of low-temperature chromizing treatment on SS316L (for 180 min at 900 °C in Ar atmosphere) to produce mainly Cr-carbide and Cr-nitride coating. The substrates were pretreated by Shot peening to active surface and reduce chromizing temperature. Results showed that chromized SS316L exhibits I_{Corr} 3×10 $^{7-}Acm^{-2}$ and ICR value 23 $m\Omega cm^2$ that are respectively, about four orders and three times lower than those of bare SS316L. Bai et al. [66, 67] used low-temperature pack chromization to form a uniform and dense chromized coating on 1045 steel using a rolling pretreatment. The results showed that the main constituent phases of the coating were carbides and the minor phases were chromium-ferric nitrides and oxides. The maximum power density of the cell manufactured with this metallic BP was higher than that of

graphitic BP. It was concluded that the performance of chromized carbon steels is comparable to that of graphite or noble metals for the application of BPs in PEM fuel cell. Furthermore, the overall cost of chromized carbon steel BPs is much lower than that of graphite or noble metals .

One of the other most common coatings on stainless steels are TiN. Zhang et al. [34] investigated the use of TiN-coated SS304 as BP. Two surface coating techniques, pulsed bias arc ion plating and magnetron sputtering, are adopted to prepare the TiN-coated stainless steel. Both the TiN and Ti_2N/TiN coatings provided low ICR, 25 and 26 $m\Omega cm^2$,respectively, and low I_{Corr}, 0.0131 and 0.0145 μAcm^{-2} ,respectively. However, the long-term test is necessary for better validation. Yoon et al. [68] evaluated a number of protective coatings deposited on stainless steel substrates (SS304, SS310, and SS316) by electroplating and physical vapor deposition (PVD) methods. The coatings include Gold (2 nm, 10 nm, and 1 µm thicknesses), Titanium, Zirconium, Zirconium Nitride (ZrN), Zirconium Niobium (ZrNb), and Zirconium Nitride with a Gold top layer (ZrNAu). The results showed that Zr-coated samples satisfied the DOE target for corrosion resistance at both anode and cathode sides in typical PEM fuel cell environments in the short-term. However, the ICR values of bare SS316L (300 $m\Omega cm^2$,(Zr-coated SS (1000 $m\Omega cm^2$,(ZrN-coated SS (160 $m\Omega cm^2$,(ZrNAu- coated SS (6 $m\Omega cm^2$-2 ,(nm-Au-coated SS (80 $m\Omega cm^2$,(-10nm-Au-coated SS (4 $m\Omega cm^2$,(and 1-µm- Au-coated SS (5 $m\Omega cm^2$ (indicated that although Zr is a suitable anti-corrosion coating, it greatly increases the ICR. Moreover, Au or Au-containing coatings can beneficially reduce I_{Corr} and ICR to lower than DOE criteria, provided that the thickness of gold coating to be higher than 10 nm (particularly for the cathode side). The above results indicate that CrN or nitrogen containing coatings, performed in the low temperatures are two favorable coatings upon stainless steel BPs of PEM fuel cells.

.3.7 Carbide based amorphous metallic coating

Natesan and Johnson [69] studied the oxidation and sulfidation of SS310 and chromium-carbide and Cr-coated alloy in high O_2 and S environment in a temperature range of 650-875 °C. The use of appropriate corrosion resistant coatings on metallic components offers an avenue to minimize material degradation and extend their lifetime. The coatings for the test were developed by an electro-spark deposition process in which short duration and high-current electrical pulses were used to deposit the electrode material on the metallic substrate. They observed that in a high sulfur environment, the uncoated alloy exhibited severe sulfidation corrosion by means of (Fe, Ni) sulfide formation; the Cr-coated alloy exhibited moderate corrosion whereas the chromium carbide-coated alloy exhibited the least corrosion. Vickers hardness measurements made by Natesan and Johnson [69] on the surface and as a function of depth showed that the initial high hardness values of chromium-carbide coated specimens were retained even after oxidation and sulfidation treatment. In another work, Hung [70] studied on coating chromium carbide on aluminum and SS316 substrates. The results of the study showed that chromium carbide coatings have relatively low ICR and moderate corrosion resistance in comparison to other metals. In addition, the result of the 1000 h lifetime testing of a single cell containing coated aluminum BPs, at cell temperature 70 °C under cyclic loading condition, showed minimal power degradation (<5%) due to metal corrosion .[70]

Conclusions

Because of its high efficiency, low-temperature operation, high-power density, and relatively fast start up, the proton exchange membrane fuel cell offers the potential for a near-zero emission power source for transportation, mobile, and stationary applications. However, for such power sources to become mainstream and gain a sizable share of the market, they must be able to compete with other power sources in terms of cost, reliability, durability, and public acceptance. Cost and durability are two major factors that have impeded the introduction of fuel cells as primary energy sources in to different sectors of the economy. Accordingly, identifying opportunities for cost reduction and cost avoidance in the selection and manufacture of the different components of PEMFCs, as well as improving their life expectancy, can significantly increase their chance of becoming a major player in the energy market. Bipolar plates play a vital role in PEMFCs in terms of operation and cost; consequently, lowering their cost and improving their performance are highly desirable. Such plates must be rigid, durable, conductive, stable in harsh environments and resist dimensional change at relatively high temperatures and under compressive loads. A significant amount of work is currently focused on developing novel materials and fabrication processes to not only meet the above goals, but also to satisfy different market requirements. Bipolar plates have traditionally been fabricated from high-density graphite on account of its superior corrosion resistance, chemical stability, high thermal conductivity, and availability. However, due to its molecular structure, it exhibits poor mechanical properties, high manufacturing cost, and it is difficult to work with. As a result, recent studies have moved away from graphite in the direction of developing and optimizing more cost effective materials such as metals and composites. Nevertheless, graphite has established itself as the benchmark material for fabrication of bipolar plates, against which all other materials are compared. Metallic bipolar plates offer higher strength and electrical conductivity, better formability and manufacturability, lower gas permeability, and better shock resistance than graphite plates. Furthermore, their unique mechanical properties allow for fabrication of thinner plates and reduced scrap rates. They are, however, more susceptible to corrosion, which can adversely impact their performance and durability. This has necessitated the need for the application of corrosion resistant coatings to reduce or eliminate these effects. Most of the research in the past has focused on iron-based alloys, such as stainless steel, because of their low costs; however, more recently, considerable efforts have been expended to use noble metals, aluminum, and titanium as the material of choice for fabricating bipolar plates. Another advantage of metallic bipolar plates over graphitic bipolar plates is the availability and maturity of a large number of manufacturing processes that are cost effective, including stamping, compression-molding, and embossing. Composite plates offer improved mechanical properties and manufacturability over graphite plates, as well as a cost reduction; however, they are inferior in terms of electrical conductivity   .

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