Research progress on bipolar plate coating for automotive fuel cells

**Abstract:**

**As one of the important components of PEMFC, the performance of the bipolar plate seriously affects the working efficiency and service life of the fuel cell. Metal bipolar plates are prone to corrosion after long-term operation, which contaminates the proton exchange membrane and leads to an increase in membrane resistance and reduces the performance of the proton exchange membrane fuel cell. In this paper, the preparation process and materials of bipolar plate coatings for automotive fuel cells are discussed in depth. The characteristics and applications of different preparation methods are elaborated in detail, and the properties and applications of various coating materials are analyzed. The study shows that the study of efficient and low-cost preparation process and high-performance coating materials is the key to improve the performance of automotive fuel cell bipolar plates, which is of great significance for promoting the commercial application of fuel cell vehicles.**

**Keywords:Bipolar plates，Surface modification，Corrosion-resistant,** **fuel cells**

**I. Introduction**

In today's society, the energy crisis is increasingly severe. The massive consumption of traditional fossil energy and the damage to the ecological environment have forced the development of clean and sustainable energy to become the focus of global attention. Proton exchange membrane fuel cells (PEMFC) are widely used in the automotive field due to their characteristics of fast start-up, high energy conversion, and environmental friendliness. Bipolar plates (BPP) are one of the core components of fuel cells, accounting for 60%-80% of the total mass of the stack and about 40% of the cost. Their main functions are to support the membrane electrode assembly (MEA), provide fluid channels for hydrogen, oxygen, and coolant, collect electrons, and conduct heat [1]. The performance of BPP plays a decisive role in the overall performance, service life, and cost of fuel cells. However, the actual operating environment of fuel cells is harsh and the working conditions are complex. They are in a humid environment at 60°C-80°C for a long time, with an internal solution pH value of 2-3, and there are corrosive ions such as ，，，and .PEMFC uses hydrogen and oxygen as fuels, and it is necessary to ensure that both can smoothly reach the membrane electrode for electrochemical reactions. To ensure the effective operation of PEMFC, bipolar plates must have excellent electrical conductivity, thermal conductivity, corrosion resistance, gas tightness, and good mechanical properties [2].

Surface modification technology can meet these requirements, by preparing a suitable coating on the surface of the bipolar plate, not only can improve the corrosion resistance of the bipolar plate, prevent it from corrosion in harsh environments and cause performance degradation, but also improve the surface conductivity of the bipolar plate, reduce the contact resistance, thereby improving the power output and energy conversion efficiency of the fuel cell[3]。 In addition, by optimizing the preparation process and coating materials, the cost of bipolar plates can be reduced to a certain extent, and the commercialization of fuel cell vehicles will be promoted. Depending on the processing method, surface modification technologies include physical vapor deposition (PVD), chemical vapor deposition (CVD), electroplating, thermal spraying and electroless plating.

Precious metal coatings in metal coatings (such as gold, silver, platinum, etc.) have been widely used in early research due to their good conductivity and corrosion resistance, but the high cost has limited their large-scale commercialization[4]。 Therefore, in recent years, the research of non-precious metal coatings (such as nickel, copper, chromium, etc.) has received more attention, and the performance of non-precious metal coatings has been significantly improved by means of alloying and surface modification[5]。 Metal compound coatings (e.g., carbide, nitride, etc.) have high hardness, high wear resistance and good chemical stability, showing great potential in improving the corrosion resistance and mechanical properties of bipolar plates[6，7]。 With its unique electrical properties and good film-forming properties, conductive polymer coatings provide a new idea for the research of bipolar plate coatings. In addition, carbon-based coatings (such as graphene, carbon nanotubes, etc.) have become one of the current research hotspots due to their excellent conductivity, high strength and good chemical stability[8]。

In this paper, various preparation processes of bipolar plate coatings are systematically introduced, and the properties of different bipolar plate coating materials are analyzed, the current research challenges are summarized, and the future development trend of bipolar plate coatings is prospected.

**2. Bipolar plate surface modification technology**

### 2.1 Physical Vapor Deposition (PVD).

Physical vapor deposition (PVD) refers to the technology of physically transforming a solid material source from one state to another and finally depositing it on a substrate[9]。 Common PVD technologies include: evaporation coating, sputtering coating, and ion plating.

Evaporative coating is one of the earliest physical vapor deposition technologies[10]。The schematic diagram of the vacuum chamber of the evaporation equipment is shown in Figure 1. The principle is that the coating material to be deposited (i.e. evaporatedSource material) is heated to evaporation temperature, so that its atoms or molecules can obtain enough energy to change from solid or liquid to gaseous state, and diffuse to the surface of the substrate in a vacuum environment, and finally deposit on the surface of the substrate to form a coating. This method can prepare a coating with high purity, because in a vacuum environment, the evaporation source material is directly deposited on the surface of the substrate after evaporation, and the coating is relatively dense and of good quality, which reduces the mixing of impurities[6]。 However, for materials with high melting points and complex bipolar plates, evaporation coating technology is no longer suitable. Evaporation coating technology is widely used in optical thin films, microelectronic fabrication, jewelry and packaging coatings[11]。 However, evaporation coating requires high-purity target materials, and the equipment cost and operation and maintenance cost are high, which limits its large-scale application。

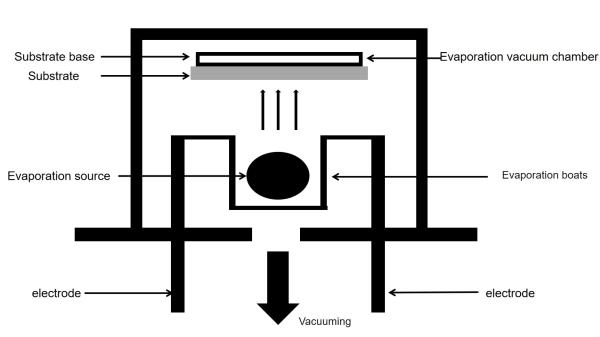


Figure 1 Sputter coating

Sputter coating is a commonly used method in physical vapor deposition.A schematic diagram of the magnetron sputtering vacuum chamber is shown in Figure 2. Its basic principle refers to the use of vacuum environmentArgon ions bombard the surface of the target, so that the atoms or molecules of the target can obtain enough energy to escape from the surface of the target and deposit on the surface of the substrate to form a coating. During sputtering, argon ions collide with target atoms, transferring part of the energy to the target atoms, causing them to sputter out of the surface binding force. Some of these sputtered atoms or molecules move irregularly in the vacuum chamber, and some of them reach the surface of the substrate, where they are adsorbed, diffused, nucleated and grown, and finally form a continuous coating[12]。 According to the different sputtering sources, common sputtering coatings include DC sputtering sources, RF sputtering sources and magnetron sputtering sources[13]。 By precisely controlling sputtering parameters such as sputtering power, sputtering time, gas flow, etc., the thickness and composition of the coating can be precisely controlled to obtain a coating with excellent performance. Secondly, sputtering coating can deposit various coating materials on the surface of bipolar plates of different materials, including metals, alloys, compounds, etc., and has a wide range of applicability. However, the high cost, relatively low deposition rate, low production efficiency, and high cost of equipment and maintenance of sputter coating technology limit its large-scale application.

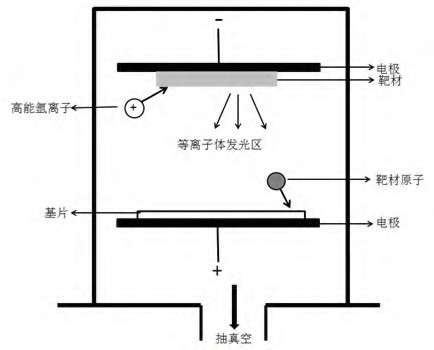


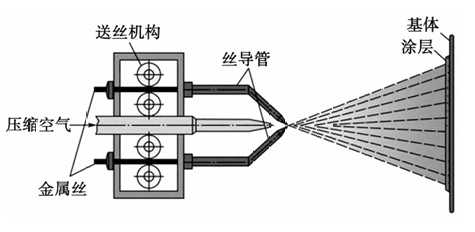
Figure 2 Schematic diagram of a magnetron sputtering vacuum chamber [9].

### 2.2 Plating

Electroplating is a kind of metal electrodeposition, and the obtained metal deposition layer not only has good physical properties, but also has a strong protective effect on the substrate[14]。 In electroplating, the anode is acted by the metal to be plated or the insoluble conductor, the cathode is acted by the plate to be plated, which are connected to the positive and negative poles of the power supply, and the electrolyte is selected by the acid solution to be plated as the majority. After the reactor is energized, the cathode undergoes a reduction reaction to precipitate the metal ions to be plated[15]。 However, due to the electroplating technology, it will produce a large amount of corrosive waste liquid and pollute the environment, and will eventually be replaced by other processes[16]。

### 2.3 Thermal spraying

The principle of thermal spraying technology is to use flame or plasma as a heat source to heat the sprayed material to a molten or semi-molten state, and atomize it through a high-speed air flow to spray on the surface of the pretreated parts to form a protective coating[14]。 This is shown in Figure 3. Thermal spraying technology is simple to operate, and the selection of materials can be metals, ceramics, etc., with a wide range, the most important of which is green and environmentally friendly, low cost and large-scale production. If the size of the part is reduced after wear or corrosion, the surface can also be repaired by thermal spray technology[18]。



digit 3 Thermal spray technology.[17]

2.3.1 Flame spraying

Flame spraying(Flame Spraying)It is a method of heating the sputtering material to a molten or semi-molten state by using a flame generated by combustible gas, etc., and atomizing it to form a coating on the surface of the substrate under the impetus of the air flow[19]。 Flame spraying is suitable for a wide range of materials, including metals and their alloys, ceramic oxides such as:Al₂O₃、Cr₂O₃etc., cermets such as WC-Co, Cr₃C₂-NiCr, etc. According to the form of spraying material, flame spraying can be divided into: powder flame spraying, wire flame spraying and bar flame spraying. Flame spraying has a low operating temperature[20]The surface of the matrix will only withstand the temperature of 200~250 °C, and the thermal deformation of the matrix is small, so its influence on the matrix is small. Compared with evaporative coating technology, the cost of flame spraying is lower, the single precipitation efficiency is also low, and about 30~50% of the material is wasted.

2.3.2 Arc spraying

Arc spraying technology (Arc sprayingThe wire material to be sprayed is used as its self-consuming electrode, and the arc formed at the end is used as the heat source[22][24]。The top of the wire melts as the temperature of the end arc increases, and the coating forms on the surface of the substrate after atomization under the action of the gas. Flame spraying technology has the advantages of high efficiency, convenient on-site construction, short construction time, low cost and good safety. However, during the spraying process, the atomized metal particles will have a large difference in size, which is caused by the accumulation caused by the melting of the metal tip.

2.3.3 Explosive spraying

Explosive Spraying (Explosives sprayingOxygen and acetylene gas are mixed in a certain proportion and then detonated in a specially designed combustion chamber to heat the sprayed particles to a molten state and form a coating on the surface of the parts at high speed. While the bond strength between the explosive spraying coating and the substrate is high, the number of pores in the coating is small, but the working noise is large, and it is difficult to spray the workpiece with complex shape and small cavity[23]。

2.3.4 Plasma spraying

The positive electrode of the battery is connected to the nozzle (anode) of the plasma spray gun, and the negative electrode is connected to the electrode (cathode), and the working gas is passed between the nozzle and the electrode, and the arc is ignited by high-frequency sparks, and the arc heats the gas to ionize it to produce a plasma arc, and the heated and expanded gas is ejected from the nozzle to form a high-speed plasma jet. The sprayed powder is heated to a molten or semi-molten state while being accelerated by a plasma jet and sprayed onto the substrate to form a coating. Plasma spraying has the advantages of easy adjustment, fast deposition rate, wide range of sprayed materials,High flame temperature and strong adaptability and many other advantages[26]。

2.3.5 Supersonic flame spraying

Supersonic Flame Spraying (High-speed Oxyen fuelThe combustion of gas such as propane and propylene and high-temperature compressed oxygen to produce a high-temperature and high-pressure flame flow is used to heat the spraying powder to a molten or semi-molten state, and the coating is formed on the surface of the workpiece at a very high speed.HVOF has better resistance to wear, corrosion and fatigueAnd the porosity of the prepared coating can reach less than 5%, which has the characteristics of compactness and bonding strength[25]。Due to its high particle velocity and low particle temperature, HVOF is particularly suitable for the preparation of coatings such as cermets, alloys and pure metals[27].

2.3.6 Thermal spraying + post-treatment process

Post-treatment is required to improve the existing coating due to the fact that the resulting coating has problems such as porosity, oxides, unmelted particles, and interlayer boundaries, which can significantly reduce corrosion resistance[14]。

As a post-treatment process, the principle of hole sealing treatment is to select the appropriate sealing agent for coating construction[28]In order to achieve a good sealing effect, the following points should be paid attention to when selecting the sealing agent:

Good permeability: It can be well filled into the slender and narrow channel of the coating, preventing the corrosive liquid from coming into contact with the substrate through the channel.

Good chemical resistance: The sealer filled in the coating needs to be selected with good chemical resistance, so as to improve the overall corrosion resistance of the coating.

Good elasticity: Since the coating often changes to a certain extent during the working process, good elasticity is required to avoid it from breaking and falling off when affected by mechanical action.

Good high temperature resistance: The coating will often work in a high temperature environment, and it needs to be avoided from melting and losing its effect in a high temperature environment.

Green: No damage to the environment.

### 2.4 Chemical Vapor Deposition (CVD)

Chemical vapor deposition (Chemical vapor deposition，Cardiovascular disease) is a surface modification technology that uses more than two gases to react chemically on the surface of the substrate and further form a protective film[29]。 In the CVD process, bipolar plates are usually placed in the reaction chamber to introduce the gaseous coating material and reaction gases into the reaction chamber. Under the action of high temperatures, plasma or catalysts, gaseous reactants undergo chemical reactions on the surface of the bipolar plate to form a solid coating material and deposit it on the surface of the bipolar plate. Conventional chemical vapor deposition technology enables the preparation of coatings with good chemical stability and uniformity[30].However, due to its high reaction temperature, it will lead to problems such as deformation and performance deterioration of metal bipolar plates at high temperatures, which limits the use.

Plasma Enhanced Chemical Vapor Deposition (PECVD)[33]Based on chemical vapor deposition, plasma is used to promote chemical reactions, and high-quality thin films can be deposited at lower temperatures[31]。 The principle is that in a vacuum environment (usually the pressure is 10-3- 102 Pa), the reaction gases (such as silane, ammonia, methane, etc.) introduced into the reaction chamber are excited and ionized under the action of a high-frequency electric field to form plasma，The high-energy electrons in the plasma collide with the reactive gas molecules, so that the gas molecules gain enough energy to enhance the chemical activity of the reactive substance，A coating is deposited on the surface of the bipolar plate[33]。 The biggest advantage of PECVD is that the reaction temperature of traditional PVD is reduced to about 100-300°C, which meets the temperature-sensitive processing environment of bipolar plate materials. The coating obtained by PECVD technology has good conductivity, large defects and pores in the coating, and the compactness and uniformity are greatly improved. Plasma enhances the chemical bonding between the film and the bipolar plate substrate and improves the adhesion of the coating.The deposition rate of PECVD is relatively fast, and a certain thickness of coating can be obtained in a shorter time, improving production efficiency.

1. **Modified coating on the surface of bipolar plates**

Commonly used bipolar plates are mainly divided into: graphite bipolar plates, composite bipolar plates, and metal bipolar plates[37]。 Graphite has excellent thermal and electrical conductivity and is regarded as an excellent material for making bipolar plates, and the bipolar plates made of graphite materials have good corrosion resistance, hydrophobicity, stability and low interfacial contact resistance. However, the brittleness and low strength of graphite make it difficult to process graphite bipolar plates. At the same time, the porosity of graphite is relatively large, and the air tightness and mechanical strength of graphite bipolar plates are relatively poor, which limits the commercialization process of graphite bipolar plates. The bipolar plate of the composite material is mainly processed by conductive polymer and conductive filler, which has the advantages of excellent conductivity, good processing formability and corrosion resistance, however, there is a phenomenon of local heating in the actual work of the fuel cell, which leads to the local temperature is too high, which limits the working temperature range of the composite bipolar plate. The metal bipolar plate has the characteristics of good electrical conductivity, thermal conductivity, easy forming, and low cost[34]In the acidic environment of fuel cells, metal corrosion will increase the interfacial contact resistance of the fuel cell and reduce the output efficiency[35]。 The most effective way to solve the problem of poor corrosion and conductivity of metal bipolar plates is to modify the surface of metal bipolar plates. At present, the surface modification coating of metal bipolar plates can be divided into three categories, namely metal-based coatings, conductive polymer coatings and carbon-based coatings[36]。

### 3.1 Metal-based coatings

Precious metal coatings, such as Au, Ag and Pt,Due to its excellent conductivity and inactivity characteristics, it meets the requirements of conductivity and corrosion resistance of metal bipolar plates. However, it is expensive and far more expensive than the fuel cell itself, and cannot be commercialized on a large scale. Wen et al[38]A layer of Au coating with a thickness of 1 μm was deposited on the surface of 316L stainless steel, and the results of the kinetic potential planning curves of 0, 12, 24 and 48 were immersed in a simulated fuel cell environment (0.5 mol/L H2SO4, 10 mg/L HF, 80 °C), respectively, as shown in Table 1. With the increase of immersion time, the reaction resistance of the specimen decreases from 3774 Ωcm2 to 1487 Ωcm2, and the self-corrosion current increases from 1.716×10-5 A/cm2 to 2.243×10-4 A/cm2, indicating that the corrosion rate increases with the development of the reaction. Due to the corrosive environment of H, SO42- and F-, electrochemical reactions occur on the gold surface, forming pitted pores and accelerating corrosion. At the same time, the local area of the film formed by the Au coating mainly contains Au and O, which reduces the corrosion tendency and leads to the increase of self-corrosion potential with the increase of soaking time.

Table 1.Fitting results of potentiodynamic polarization curves[38]

|  |  |  |
| --- | --- | --- |
| Time (h) | Corrosion potential (V) | Corrosion current (A/cm2) |
| 0 | -0.278 | 1.716×10-5 |
| 12 | -0.335 | 3.757×10-5 |
| 24 | -0.324 | 4.169×10-5 |
| 48 | -0.256 | 2.243×10-4 |

Feng Kai et al[39]A thin layer of Ag coating was injected into the surface of 316L stainless steel by ion implantation, and electrochemical experiments were carried out, and the corrosion current density of the 316L stainless steel was compared with that of the unmodified metal bipolar plate in the potentiostatic test results10 μA·cm-2 is reduced to 0.7 μA·cm-2, and its interface contact resistance ICR is from 312.8mΩ·cm-2 was reduced to 78.8 mΩ·cm-2。 In order to avoid excessive costs, precious metals are now mostly present in the coating in the form of doping. Jin et al. prepared Cr-C coatings on the surface of 316L stainless steel by using cathodic plasma electrolytic deposition (CPED) technology, and studied the effects of trivalent chromium salt concentration in the plating solution and deposition time on the microstructure and composition of the Cr-C coatings. The research shows that increasing the chromium salt concentration and prolonging the deposition time can improve the corrosion resistance of the Cr-C coatings in two environments, but will slightly reduce their surface conductivity. The optimal Cr-C coating obtained by deposition for 60 minutes under the chromium salt concentration of 60 g·L⁻¹ can be spontaneously passivated. In the simulated PEMFC anode and cathode environments, after potentiostatic polarization at -0.1 Vₛce and 0.6 Vₛce for 5 hours, the current densities are about -0.03 μA·cm⁻² and 0.3 μA·cm⁻² respectively, and the ICR value is lower than 6 mΩ·cm². It is of great significance to improve the CPED process for Cr-C coatings on stainless steel bipolar plates[40].

Precious metal materials are not suitable for the surface modification of bipolar plates, and some alloy materials have begun to become new research directions. Zhang et al. used pulsed polarized arc ion plating (PBAIP) to prepare a layer of Ti-Ag coating on a titanium substrate, and the point chemical experiments proved that the conductivity of the modified coating was significantly enhanced, and the interfacial contact resistance at 1.4 MPa was only 4.3 mU cm2. , which exhibits excellent corrosion resistance, due to the fact that the Ti-Ag coating combines the advantages of both elements, guaranteeing excellent corrosion resistance while having good electrical conductivity. Fan etc[41]By comparing TiN/SS and Au/TiN/SS, it was found that the corrosion current density decreased slightly, and the ICR decreased from 5.48 mΩ·cm2 to 1.47 mΩ·cm2, indicating that Au microdots not only helped to inhibit further oxidation on the surface of the coating and hinder the corrosion, but also provided additional channels for electron transfer. Xin et al[42]The new coating is found to be denser, and the stability of Cr2O3 is improved due to the residual boride, so that the Ni20Cr4B coating has excellent thermal corrosion resistance at 600°C. According to the thermodynamic calculations, this experimental phenomenon is expected to be applied to other alloys, such as Fe, Cu, Mn, etc.

Unlike traditional carbon-based, nitrogen-based coatings, MAX phase coatings are a new type of ceramic coating. The MAX phase has a unique layered hexagonal crystal system, and the different layers are closely connected by the metallic bonds of M atoms and A atoms, M is a pretransition group metal, such as Ti, Ni, Cr, etc., A is a group III.B and IV.B group elements, such as Al, Si, etc., and X is mainly C and N. Unlike the chemical bonds in ceramic materials, the MAX phase has mixed covalent-ionic-metallic properties, so it has both metallic properties, such as good electrical and thermal conductivity, machinability, low hardness, and excellent corrosion, heat, and oxidation resistance.

Abbas et al[43]The Ti2AlC coating was prepared by magnetron sputtering technology at different temperatures, and it was found that with the increase of temperature to 750°C, the coating showed better conductivity, and the coating deposited at 750°C had a very low ICR, which was only 3.27 mΩ·cm2, which was much lower than the DOE standard(See Figure 4)。

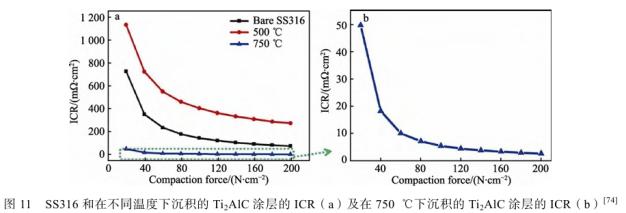


Fig.4. ICR (a) of SS316 and Ti2AlC coatings deposited at different temperatures and Ti2AlC coatings deposited at 750°C (b)[43]

Lu et al[44]Ti3AlC2 MAX phase coating was prepared by magnetron sputtering and heat treatment. The results show that with the formation of the MAX phase, the corrosion resistance and electrical conductivity of the coating are improved, and the contact resistance is only 3.725mΩ·cm2, which meets the requirements of the DOE standard. Among the MAX phases, Cr2AlC has attracted much attention due to its excellent oxidation resistance and corrosion resistance, as well as its simple preparation process. At the same time, the thermal expansion coefficient of Cr2AlC is similar to that of SS316L, which is conducive to improving the good adhesion between the substrate and the coating. Ma et al[45]The cathode arc composite magnetron sputtering method was used to prepare Cr-Al-C coating on the surface of SS316L. Electrochemical tests and ICR tests show that the coatings with different annealing times show excellent corrosion resistance and electrical conductivity, and the interface contact resistance is much smaller than that of bare boards. Liu Yun et al[46]The results show that the corrosion current density of the coating is 2.43×10−7A/cm2, which is 2 orders of magnitude lower than that of SS304. The anode current density density after potentiostatically polarized is stable at 2.3×10−7A/cm2，The cathode current density also decreases to 2.44×10−8A/cm2, indicating that the Cr2AlC coating is also beneficial to improve the corrosion resistance of SS304 bipolar plates. Transition metal carbide and nitride coatings have been increasingly studied, and their corrosion resistance has been greatly improved, and the continuous progress of preparation technology has also made full use of their good mechanical properties.

Combined with the above experiments, the corrosion current density of Cr₂AlC coating is 2.43×10⁻⁷A/cm²< Ti-Ag coating< Ag ion implantation coating (7×10⁻⁷A/cm²) < unmodified 316L stainless steel (1×10⁻⁵A/cm²). The interfacial contact resistance of the Ti-Ag coating (4.3 mΩ・cm²), <the Ti₂AlC coating (3.27 mΩ・cm²), <the Ti₃AlC₂ coating (3.725 mΩ・cm²<), the Au/TiN coating (1.47 mΩ・cm²<), the Ag ion implantation coating (78.8 mΩ・cm²), < the unmodified 316L stainless steel (312.8 mΩ・cm²) . Precious metal coatings have good conductivity and initial corrosion resistance, but the long-term increase in corrosion rates (e.g., Au coatings) and the high cost are only suitable for use in doped form (e.g., TiN-Ag). The alloy coating balances conductivity and corrosion resistance through the synergy of elements (e.g., Ti-Ag, TiN/Au), and the ICR and corrosion current density are better than those of pure precious metal coatings, resulting in lower costs. MAX phase coatings have the best comprehensive performance, especially Cr₂AlC, Ti₂AlC, etc., which not only have very low corrosion current density (strong corrosion resistance), but also have ICR far lower than the standard (good conductivity), and moderate cost, which is the direction with the most potential for commercialization.

### 3.2 Conductive polymer coating

In addition to the preparation of metal-based coatings on metal bipolar plates, relevant researchers have also prepared conductive polymer coatings for surface modification of metal bipolar plates. S. J. Narasimharaju[47] et al. investigated the efficacy of polypyrrole (PPy) coatings enhanced with chromium nitride (CrN) nanoparticles (NPs) on 6061 aluminum alloy (AA) specimens. These coatings significantly improved the corrosion resistance, polarization resistance, and protection efficiency of 6061 AA. Among all the tested coatings, the PPy-CrN0.2 coating performed the best, with a significantly low corrosion current (Icorr) of 0.44 µA/cm². This coating also had the highest polarization resistance value of 47,904.53 Ω/cm² and an impressive protection efficiency of 72.84%, surpassing other coated specimens. At a compaction pressure of 1.4 MPa, the PPy-CrN0.2 coating exhibited the lowest interfacial contact resistance (ICR) of 18.4 mΩ/cm², confirming its improved conductivity and suitability for proton exchange membrane fuel cells. Li et al[48]In the same way that he studied the rGO-PANI double-layer protective coating, he introduced O2 into the PEMFC cathode working environment to study the corrosion performance and found that the continuous dense rGO coating on the porous PANI improved the corrosion resistance of the bipolar plates. Oxygen has a significant effect on the corrosion resistance of rGO/PANI/316L SS, which helps to form a protective passivation film at the membrane/substrate interface, and improves the corrosion resistance of rGO/PANI/316L SS bipolar plates.Qi[49] et al. functionalized graphene with p-aminobenzoic acid and p-phenylenediamine to enhance its compatibility with polyaniline while maintaining the electrical conductivity of graphene at approximately 169 S/cm. During the in-situ polymerization of the functionalized graphene/polyaniline composites, the electrical conductivity varied significantly between 41 - 91 S/cm due to changes in the surface functional groups of graphene. Subsequently, the relevant composite coatings were prepared on the surface of 316L stainless steel via centrifugal spraying. The interfacial contact resistance of these coatings was comparable to that of gold coatings, but their corrosion current density was relatively high due to the presence of hydrophilic groups. After post-treatment to consume some amino groups, the corrosion current density of the coatings decreased.Yu[50] et al. used a new pulse electrodeposition method to prepare dense polyaniline (PANI) coatings and polyaniline/carbon nanotube (PANI/CNTs) composite coatings on the surface of 316 stainless steel bipolar plates for proton exchange membrane fuel cells. The results showed that compared with the PANI coating, the corrosion potential of the PANI/CNTs composite coating increased by approximately 78 mV, and the corrosion current density decreased by an order of magnitude. At the working potential of 0.6 V (vs. SCE), the current density of the PANI/CNTs coating dropped to about 1.9 μA·cm⁻². After a 5-hour potentiostatic test, there was no obvious corrosion on the coating surface. The interfacial contact resistance (ICR) of the PANI/CNTs coating was 35% lower than that of the PANI coating, and after the polarization process, the contact resistance of the PANI/CNTs coating remained lower than that of the PANI coating. Due to the improved corrosion resistance and electrical conductivity, the PANI/CNTs coating is more suitable for the protection of bipolar plates.

Conductive polymer coatings have excellent physical and chemical stability and provide effective protection. In the future, conductive polymer coatings with good corrosion resistance and electrical conductivity applied to metal bipolar plates have certain application prospects.

### 3.3 Carbon-based coatings

Carbon-based coatings and their modified carbon-based coatings have excellent electrical conductivity and corrosion resistance, and are suitable for large-scale commercial production, and have broad application prospects in the surface modification of metal bipolar plates. Gong[51] et al. employed magnetron sputtering to deposit a chromium/tungsten/diamond-like carbon (Cr/W/DLC) multi-layer coating on titanium alloy (TC4) surfaces, aiming to enhance the electrical conductivity, corrosion resistance, and coating adhesion of bipolar plates. Tests revealed that at potentials of 1.2 V, 1.5 V, and 1.8 V, the potentiostatic polarization current densities were 0.11 μA·cm⁻², 0.19 μA·cm⁻², and 0.4 μA·cm⁻², respectively, significantly lower than those of the TC4 substrate and exhibiting long-term stability. Under a contact pressure of 1.4 MPa, the interfacial contact resistance measured 16.98 mΩ/cm². These results indicate that the coating demonstrates both excellent corrosion resistance and good electrical conductivity under the operating conditions of proton exchange membrane water electrolysis (PEMWE) systems. Wang et al[52]Through the magnetic filtration vacuum cathode arc deposition technology SS304 stainless steel surface deposition TiC/a-C:H composite coating, the effects of different deposition energies on the corrosion resistance and conductivity of the coating were studied, and it was found that under the negative bias pressure of -100 to -500 V substrate, the coatings were all dense coatings with few defects. With the increase of the negative bias value, the nanocrystalline size of the coating increases, and when the negative bias voltage is -100V, the ICR value is 1.49 mΩ/cm2, and the current density is 5.25×10-8 μA/cm2, which meets the requirements of DOE 2025。

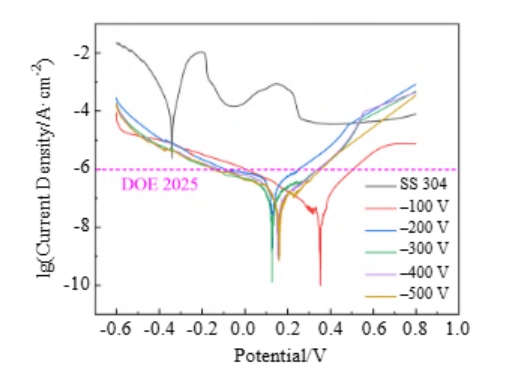


Figure 5 Vb=-Potentiodynamic polarization curves of nc-TiC/a-C:H coatings and SS304 deposited at 100~-500V[52]

Zhou Qinghuan and others[53]The magnetron sputtering method was used to control the sputtering time of the graphite target to achieve the deposition of graphite coatings of different thicknesses on 316L stainless steel metal bipolar plates, and the best thickness of graphite coatings was determined by comparing the performance of different thicknesses of graphite coatings under the same fuel cell working environment. Experiments have proved that all graphite coatings can improve the corrosion resistance and electrical conductivity of 316L stainless steel; By comparison, the optimal thickness of the graphite coating was 400 nm.Liu et[54] al. directly fabricated a reduced graphene oxide-amorphous carbon composite coating (rGO-ACC) on a 316L stainless steel substrate via a one-step reduction method using a choline chloride-ethylene glycol deep eutectic solvent (DES) dispersed with graphene oxide. In a simulated proton exchange membrane fuel cell (PEMFC) environment, potentiodynamic and potentiostatic polarization tests revealed that the corrosion current density of the rGO-ACC-coated 316L stainless steel was on the order of 10⁻⁷ A·cm⁻², indicating a significant enhancement in corrosion resistance and excellent electrochemical stability. Meanwhile, due to the outstanding electrical conductivity of the reduced graphene oxide (rGO) within the coating, the interfacial contact resistance (ICR) of the coated stainless steel was notably reduced compared to bare 316L steel. These results suggest that depositing rGO-ACC on steel surfaces could be a highly promising modification approach for PEMFC metal bipolar plates.Lee et al[55]Carbon-based composite bipolar plates with different carbon black mass fractions were prepared by compression molding method using graphite powder, carbon black as conductive filler and epoxy resin as polymer matrix. The measurement found that the conductivity of the composite bipolar plate increased with the increase of the mass fraction of the carbon black. This is due to the fact that carbon black particles are much smaller in size than graphite, and it can act as a conductive agent between graphite particles. When the mass fraction of carbon black exceeds 15%, the conductivity begins to decrease. Li et[56] al. deposited Ti-doped α-C/α-C multilayer coatings on 316L stainless steel using DC-balanced magnetron sputtering. The porosity of the coating gradually decreased from 4.54% (1 layer) to 0.21% (4 layers). At a potential of 0.6 V, the passivation current density dropped to 0.22 μA/cm², with performance significantly exceeding the target values. In addition, the introduction of the Ti-doped α-C layer further promoted the sp² hybridization of the coating. Under a pressure of 1.4 MPa, its interfacial contact resistance (ICR) value gradually decreased from 5.28 mΩ·cm² (1 layer) to 2.28 mΩ·cm² (4 layers). Therefore, this multilayer composite structure coating significantly enhances the conductivity and corrosion resistance of 316L stainless steel bipolar plates, and has higher practical value in the commercial application of proton exchange membrane fuel cell technology.

However, the residual stress between the carbon-based coating and the metal matrix weakens the coating adhesion, and the corrosion process of the coating with defects such as cracking and peeling occurs, which seriously affects its service life and hinders its practical application value.

## conclusion

At present, significant progress has been made in the research of fuel cell bipolar plate coating at home and abroad, new coating materials are emerging, the preparation process is continuously optimized, the performance is continuously improved, and the commercial application is gradually advancing. In terms of cost control, many advanced coating preparation processes, such as magnetron sputtering and chemical vapor deposition (CVD) in physical vapor deposition (PVD), are expensive to use and maintain high costs. Productivity is another key issue that needs to be addressed in the preparation process. The deposition rate of some coating preparation processes is low, and the preparation cycle is long, which is difficult to meet the needs of large-scale industrial production. In this paper, the preparation process and materials of bipolar plate coatings for automotive fuel cells are discussed in depth, the different preparation processes are analyzed in detail, the scope of application and advantages of each process are clarified, and the selection of processes in practical applications is provided with favorable arguments, and the properties of various coating materials such as metal coatings, conductive polymer coatings and carbon-based coatings are analyzed in depthThe performance of different coatings was analyzed through related research experiments, which provided a theoretical basis for the selection and design of coating materials. In short, the current research on bipolar plates has a long way to go, and the research and development of new preparation processes and new materials, as well as new testing methods for materials, are still the development direction of the scientific research team.

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1.

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3.

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