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ADVANCEMENTS IN THE PREPARATION AND APPLICATION OF TI/TIN/DLC COATINGS FOR ENHANCING THE PERFORMANCE OF BIPOLAR PLATES IN PROTON EXCHANGE MEMBRANE FUEL CELLS (PEMFCS): A REVIEW

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Abstract

Proton exchange membrane fuel cell has attracted much attention in recent years due to their advantages of environmental protection and high resource utilization, which is important for improving the global environment. Bipolar plates are the important components of fuel cell, which accounts for most of the weight and high cost. Compared with graphite bipolar plates, metal bipolar plates are easier to machining and have lower cost because of its good mechanical properties. However, in the acidic environment of proton exchange membrane fuel cell operation, metal bipolar plates are prone to corrosion, which leads to lower output efficiency of fuel cell and seriously affected the application. Applying a protective coating to the metal bipolar plates is an effective way to improve its corrosion resistance. This paper mainly introduces the research progress of several anti-corrosion coatings for metal bipolar plates in recent years, and summarizes the challenges.

Keyword:* *Corrosion resistance, Conductivity, Titanium bipolar plates, Metallic coatings

1.INTRODUCTION

Proton Exchange Membrane Fuel Cells (PEMFCs) are a type of fuel cell technology that converts chemical energy from hydrogen into electrical energy, with water and heat as the only byproducts. They consist of several key components such as the anode, where hydrogen gas is split into protons and electrons by a catalyst; the cathode, where oxygen reacts with protons and electrons to form water; and the electrolyte (proton exchange membrane), which allows only protons to pass through while blocking electrons. PEMFCs operate at relatively low temperatures (60–100°C), making them efficient, compact, and suitable for various applications, including electric vehicles, stationary power generation, and portable devices. They are considered a clean energy source, as their only emissions are water and heat. The study of PEMFCs has gained significant attention due to their diverse applications in chemical sensors, batteries, supercapacitors, and power generation, leading to the development of membrane-electrode assemblies (MEAs) for various fuel cell types. PEMFCs are considered highly efficient electrochemical devices with high power density, low emissions, and effective energy supply. Compared to Redox Flow Batteries (RFBs), PEMFCs offer advantages such as the absence of liquid components (ideal for mobile devices), no toxic materials outside the cell, no precipitation reactions limiting energy density, and greater long-term stability without issues like electrolyte evaporation, instability, or dendritic metal growth. PEMFCs offer a promising and environmentally friendly alternative for powering vehicles and other devices. The main challenge in commercializing PEMFCs is the high manufacturing cost, with 90% of the total cost attributed to bipolar plates and MEAs. Reducing the cost and improving the performance of these components is essential for commercial viability. Key challenges include power density, cost, and weight of the PEMFC stack. Metals are promising candidates for bipolar plates due to their mechanical stability, electrical conductivity, and ease of shaping for flow channels. However, they are prone to corrosion and dissolution in the acidic environment (pH 2–3) and temperatures around 80°C, leading to increased electrical resistance and reduced power output [1]. To address this, metal plates are often coated with protective layers.

Bipolar Plates (BPs) are crucial components in PEMFC stacks, accounting for 60–80% of the total stack materials. They enable electricity generation by converting hydrogen and oxygen into electrical energy. Typically made from conductive metallic, carbon, or polymeric materials, bipolar plates are essential for PEMFCs used in automotive applications. Metallic materials like stainless steel are commonly used due to their low cost and high stability [2]. Key performance metrics for bipolar plates include electrical conductivity (>100 S/cm^{-1}), flexural strength (>25 MPa), impact strength (>40.5 J/m^{-1}), thermal conductivity (>10 $Wm^{-1}{\cdot}K^{-1}$), interfacial contact resistance (<10 $m\Omega{\cdot}cm^2$), and corrosion resistance current densities (<1 mA/cm^2), all aligned with DOE targets [3]. Various physical and chemical properties are combined to create novel bipolar plates. For instance, inserting copper or aluminum mesh into hybrid polymer composite plates increased electrical conductivity from 156 S cm^{-1} to 643 S cm^{-1} and thermal conductivity from 22.7 m^{-1} K^{-1} to 30.0 m^{-1} K^{-1}. This improvement enhances stability, as metal mesh composites outperform plain materials in terms of current density and resistance. Metallic bipolar plates, ideal for thinner designs, also facilitate efficient gas flow between the anode and cathode through CNC-machined flow channels. Studies show that austenitic and ferritic SS are suitable due to their high thermal and electrical conductivities, offering high-volume, cost-effective manufacturing [4]. However, there is less study on the integration of Ti/TiN/DLC coatings in BPs. The combination or integration of Ti/TiN/DLC coatings in bipolar plates could a significant advancement in PEMFC technology. These coatings could address key performance issues, including corrosion resistance, electrical conductivity, and ICR, thereby enhancing the efficiency and durability of PEMFCs. As research and development continue, the optimization of these coating systems could holds promise for further improvements in fuel cell performance. Therefore, this review seeks to investigating the long-term stability of Ti/TiN/DLC coatings, optimizing coating thickness and deposition parameters, developing cost-effective manufacturing techniques, and evaluating the environmental impact of these coatings. Achieving these goals will enhance the performance, durability, and commercial viability of PEMFCs.

2. OVERVIEW OF TI/TIN/DLC COATINGS FOR BIPOLAR PLATES

Ti/TiN and Ti/DLC coatings are highly suitable for PEMFC bipolar plates due to their combination of corrosion resistance, electrical conductivity, and mechanical strength. Titanium provides structural integrity, while TiN significantly enhances corrosion resistance, making the plates durable in harsh fuel cell environments. DLC coatings improve electrical conductivity and reduce interfacial contact resistance (ICR), which boosts fuel cell efficiency. Additionally, DLC's wear resistance strengthens the mechanical properties of the plates, allowing them to withstand operational stresses. The synergistic effects of these coatings result in a highly efficient, durable, and long-lasting material for PEMFC bipolar plates, improving overall fuel cell performance.

2.1 Properties and advantages of Titanium (Ti) coatings

Titanium coatings offer a combination of high strength, superior corrosion resistance, and biocompatibility, making them ideal for a variety of applications, from medical implants to automotive parts. These coatings also provide excellent durability, wear resistance, and aesthetic appeal. Key advantages include a high strength-to-weight ratio, as titanium alloys are about 40% lighter than steel but can match its tensile strength. Titanium's ability to form a passive oxide layer enhances its corrosion resistance, often surpassing that of stainless steel, particularly in chloride-rich or marine environments. Additionally, titanium coatings maintain their strength at high temperatures, with some alloys performing well up to 600°C, and they are non-magnetic, making them suitable for sensitive applications. Their biocompatibility makes them non-toxic and well-suited for medical uses, while their hardness and durability protect against scratches and wear. The coatings also offer a variety of color options, allowing for both functional and decorative finishes. These properties make titanium coatings highly versatile, ensuring longer lifespans, reduced weight, and improved performance in fields such as aerospace, biomedical, and engineering.

The performance of titanium-based coatings in biomedical and energy applications has been widely studied, revealing critical insights into their corrosion resistance and durability. For biomedical applications, coatings such as Ti, TiN, TiO_2, and N–TiO_2 demonstrate varying levels of corrosion resistance when exposed to simulated body fluid (SBF). The Ti coating exhibits good adhesion and stability, with a corrosion current density (I_corr) of 5.37×10^{-7} A/cm², attributed to the formation of a protective TiO_2 layer. TiN, with a significantly lower I_corr of 7.24×10^{-8} A/cm², performs excellently by hindering ion diffusion through its compact ceramic structure [5]. TiO_2, showing an I_corr of 1.74×10^{-7} A/cm², maintains high chemical stability through its stable oxide film, while the N–TiO_2 coating, with the best corrosion resistance (I_corr of 5.25×10^{-8} A/cm²), benefits from a multilayered structure that offers superior protection [5]. Wang et al. [5] developed a lightweight, corrosion-resistant bipolar plate using titanium as a substrate due to its low manufacturing cost. Gold plating on titanium prevents oxide layer formation, offering high resistance at 40°C and maintaining stability at membrane humidifier temperatures (80–90°C). Ahmad et al. [6] utilized titanium foam, derived from pure titanium, for PEMFC bipolar plates, optimizing electrical conductivity (336.227 ± 240.61 S/cm) through the Taguchi method by adjusting composition, sintering temperature, heating rate, and soaking time. Soma et al. [7] tested titanium as a bipolar plate under simulated PEFC conditions, noting high charge transfer and contact resistance at a cathode potential of 0.64 V, but the opposite result at an anode potential of -0.36 V. To improve the performance of uncoated stainless steel (SS) and titanium in fuel cells, modification or protective coatings are necessary to enhance their corrosion resistance in the PEMFC environment.

In energy applications, particularly in proton exchange membrane (PEM) fuel cells and water electrolysis, uncoated titanium and its coatings display significant differences in performance. Uncoated Ti in PEM fuel cells shows poor corrosion resistance with an I_corr of 396 mA cm^{-2}, leading to high ohmic loss. Conversely, TiN-coated Ti exhibits a notable improvement with an I_corr of 799 mA cm^{-2}, effectively protecting against corrosion and maintaining good conductivity [8]. In PEM water electrolysis, uncoated TA1 titanium exhibits severe pitting corrosion with an I_corr of 9.57 μA cm^{-2}, whereas coatings such as Ti, Ta, and Nb significantly enhance performance. Ti-coated TA1 has a reduced I_corr of 1.41 μA cm^{-2}, offering better corrosion resistance, though still inadequate compared to other coatings [9]. Ta-coated TA1 shows a corrosion resistance of 0.48 μA cm^{-2}, but suffers from poor conductivity due to a porous Ta_2O_5 film. The Nb-coated TA1 demonstrates the best performance with the lowest I_corr of 0.02 μA cm^{-2}, due to the conductive NbO_2 in its passive film, offering excellent corrosion resistance and low internal cell resistance [9]. Overall, titanium-based coatings significantly improve corrosion resistance in both biomedical and energy applications. The combination of compact, multilayered, or conductive oxide films plays a crucial role in enhancing durability and performance, particularly in environments prone to corrosion.

Table 1. Consolidated Multi-Study of Titanium-Based Coatings for Biomedical and Energy Applications.

Coating Type	Application	Key Performance Metric	Performance Value	Key Durability/Performance Findings	Reference
Ti	Biomedical (SBF Corrosion)	Corrosion Current Density (I_corr)	5.37×10^{-7} A/cm²	Good adhesion and stability; forms protective TiO_2 layer.	[5]

TiN	Biomedical (SBF Corrosion)	Corrosion Current Density (I_corr)	7.24×10^{-8} A/cm²	Excellent; compact ceramic layer hinders ion diffusion.	[5]
TiO_2	Biomedical (SBF Corrosion)	Corrosion Current Density (I_corr)	1.74×10^{-7} A/cm²	High chemical stability from stable oxide film.	[5]
N–TiO_2	Biomedical (SBF Corrosion)	Corrosion Current Density (I_corr)	5.25×10^{-8} A/cm²	Best overall. Multilayered structure provides superior barrier.	[5]
Uncoated Ti	PEM Fuel Cell	Current Density @ 0.6 V	396 mA cm^{-2}	Poor; corrodes in fuel cell environment, leading to high ohmic loss.	[8]
TiN-coated Ti	PEM Fuel Cell	Current Density @ 0.6 V	799 mA cm^{-2}	Good; protects against corrosion, maintains conductivity, performance is ~69% of graphite.	[8]
Uncoated TA1 (Ti)	PEMWE Bipolar Plate	Corrosion Current Density (I_corr)	9.57 μA cm^{-2}	Severe pitting corrosion; forms a resistive oxide film.	[9]
Ti-coated TA1	PEMWE Bipolar Plate	Corrosion Current Density (I_corr)	1.41 μA cm^{-2}	Forms micropores during initial passivation; better than bare Ti but inadequate.	[9]
Ta-coated TA1	PEMWE Bipolar Plate	Corrosion Current Density (I_corr)	0.48 μA cm^{-2}	Good corrosion resistance, but poor conductivity (ICR) due to porous Ta_2O_5 film.	[9]
Nb-coated TA1	PEMWE Bipolar Plate	Corrosion Current Density (I_corr)	0.02 μA cm^{-2}	Best performance. Excellent corrosion resistance and lowest ICR due to conductive NbO_2 in the passive film.	[9]

2.2 Diamond-Like Carbon (DLC) coatings: structure, properties, and benefits

Diamond-Like Carbon (DLC) coatings are amorphous carbon materials with a hybrid sp^2 (graphitic) and sp^3 (diamond-like) bonding structure, providing a unique combination of properties. DLC coatings also offer a low coefficient of friction, reducing energy loss and wear in moving parts. Their chemical inertness ensures excellent resistance to corrosion and oxidation, making them suitable for harsh environments. Additionally, DLC coatings are biocompatible, non-toxic, and widely used in medical applications, such as implants and surgical tools. Depending on the formulation, DLC can also be optically transparent, making it ideal for protective coatings in optical devices. The benefits of DLC coatings are vast. They significantly enhance the durability and lifespan of components, reducing the need for maintenance and replacement. In harsh conditions, such as those involving high temperatures or corrosive environments, DLC coatings improve performance and reliability. Their low friction properties boost energy efficiency in mechanical systems, which is valuable in industries like automotive and aerospace. The biocompatibility of DLC also makes it an excellent choice for medical devices, reducing the risk of inflammation or rejection. Furthermore, their durability contributes to sustainability by reducing waste and improving energy efficiency.

The fundamental structure of DLC coatings is defined by the hybridization states of its carbon atoms and the potential inclusion of hydrogen. Carbon atoms in DLC bond in two primary ways: sp^3 hybridization, a tetrahedral bond as found in diamond that confers hardness, strength, and chemical stability; and sp^2 hybridization, a trigonal bond as found in graphite that contributes to electrical conductivity and lubricity.

Furthermore, hydrogen can be incorporated into the amorphous carbon matrix, terminating dangling carbon bonds and significantly influencing properties by reducing internal stress and modifying surface energy. The specific characteristics of a DLC coating are ultimately determined by the ratio of sp^3 to sp^2 bonds and its hydrogen content, a relationship best visualized using a ternary phase diagram. Figure 1 classifies DLC into types such as ta-C (tetrahedral amorphous carbon, hydrogen-free with high sp^3 content), a-C (amorphorphous carbon with lower sp^3 content), a-C:H (hydrogenated amorphous carbon), and ta-C:H (a hydrogenated form with high sp^3 content).

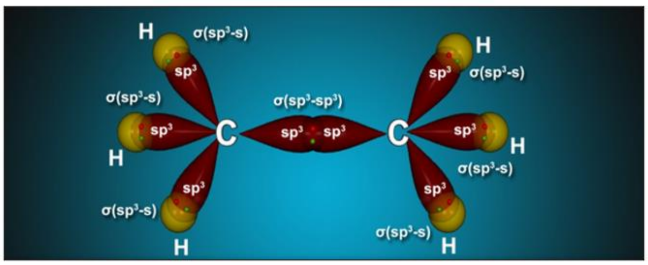

Figure 1. Schematic representation of DLC sp^3 hybridization

This amorphous yet tunable composition gives rise to a remarkable set of properties. Mechanically and tribologically, DLC coatings are defined by high hardness and exceptional wear resistance where a mere 2 µm ta-C coating can extend the lifespan of stainless steel from one week to 85 years coupled with a very low friction coefficient (as low as 0.01) that minimizes energy loss. While excellent adhesion is a key challenge, it is successfully achieved through intermediate adhesive layers of silicon, chromium, or titanium. Chemically, DLC is highly inert, acting as an effective barrier against acids and alkalis to protect substrates from corrosion. Thermally, the high intrinsic compressive stress that can lead to delamination is managed via adhesive interlayers, alloying elements, or high-energy pulsed deposition. Additional beneficial properties include a high refractive index that exceeds even diamond in some ta-C films, making them useful in optics, and a proven biocompatibility that prevents blood clotting and avoids immune responses, rendering DLC suitable for biomedical implants and surgical tools.

3. PREPARATION METHODS FOR TI/TIN/DLC COATINGS

In the past decade, various techniques have been employed for depositing multilayer coatings. The deposition techniques that have been widely used for the fabrication of multilayer coatings may be divided into two broad categories: chemical vapor deposition (CVD) and physical vapor deposition (PVD). To determine the most suitable deposition technique for the fabrication of a multilayer coating for a given material, the effects of the deposition technique on the mechanical and tribological properties of each individual layer should be considered. Though both PVD and CVD techniques have been employed for multilayer coating deposition, the preference seems to be toward PVD techniques. There are also some studies have reported using a combination of both CVD and PVD processes to fabricate multilayer coatings.

3.1. PVD and CVD methods for Ti coatings

Titanium coatings can be applied using techniques such as Physical Vapor Deposition (PVD) and Chemical Vapor Deposition (CVD). These methods allow for the creation of thin, uniform coatings on various substrates. Ti coatings provide excellent corrosion resistance, high hardness, and improved wear resistance, making them suitable for applications in aerospace, automotive, and medical devices.

3.2. PVD techniques for Ti and TiN coatings

TiN coatings are commonly deposited using PVD methods, including sputtering and arc evaporation. These techniques enable the formation of hard, wear-resistant coatings on cutting tools and other components. TiN coatings exhibit high hardness (approximately 2000–2500 HV), good thermal stability, and resistance to oxidation. They are particularly effective in machining applications, enhancing tool life and performance. TiN is widely used in cutting tools, molds, and dies due to its excellent wear resistance and ability to withstand high temperatures [10].

3.3. CVD methods for DLC coatings

DLC coatings are typically applied using techniques such as CVD and magnetron sputtering. In order to obtain multilayer coatings with good adhesion, mechanical and tribological properties using the CVD process, a relatively high substrate temperature is usually required (>200 ° C). Therefore, the materials that can be used as substrate in the CVD process are limited because their properties can be altered at elevated temperatures in some cases (e.g., polymers and some metals). These methods allow for the creation of amorphous carbon coatings with diamond-like properties. DLC coatings are known for their exceptional hardness (up to 5000 HV) and low friction coefficient (0.1–0.2), making them ideal for applications requiring minimal wear and friction. DLC is particularly effective in low-temperature, high-speed machining of soft metals like aluminum and copper, as well as in medical devices and automotive components where reduced friction is critical.

3.4. Hybrid coatings and multilayer structures

Recent advancements have led to the development of hybrid coatings, such as TiN/DLC and AlTiN/DLC, which combine the benefits of different materials. These multilayer coatings can enhance wear resistance and reduce friction simultaneously. Hybrid coatings often exhibit improved mechanical properties, such as increased hardness and better adhesion to substrates, making them suitable for demanding applications in cutting and machining [10, 11].
The choice of coating method and material depends on the specific application requirements, including wear resistance, thermal stability, and friction characteristics. Understanding the properties and performance differences of Ti, TiN, and DLC coatings enables manufacturers to select the most suitable options for their needs, ultimately enhancing tool life and production efficiency.

4. PERFORMANCE EVALUATION AND MECHANISMS BEHIND THE ENHANCEMENT OF COATED BIPOLAR PLATES

Performance evaluation of coated BPs typically involves both potentiostatic and potentiodynamic measurements to assess corrosion rates and electrical properties. These methods allow researchers to simulate fuel cell conditions and determine the effectiveness of different coatings in real-world applications. BPs are essential components in PEMFCs, serving multiple functions such as distributing reactant gases, collecting current, and facilitating water removal. However, the inherent corrosion susceptibility of metal BPs under acidic conditions necessitates the application of protective coatings to improve their performance and longevity [12].

4.1 Corrosion resistance under operating conditions

Various coatings, including noble metals, carbides, nitrides, and composite coatings, have been developed to enhance the corrosion resistance of metal bipolar plates. These coatings help meet the U.S. Department of Energy (DOE) targets for corrosion current, which should be less than 1 μA/cm^2 under operational conditions. TiN and CrN, exhibit high corrosion resistance and conductivity, ideal for BP coatings [13]. They contain free electrons forming conductive channels, mitigate corrosion, and PVD coatings are studied for corrosion resistance, thermal stability, and tribological properties [14]. Multi-arc ion plating, a PVD technique, enables rapid, low-temperature deposition of dense structures [13]. Hu et al. deposited TiN on 316L via cathodic arc deposition, with few defects improving BP performance [15]. In the simulated PEMFC anode environment (0.1 M H_2SO_4 air and 80 °C H_2SO_4 solution), PANI could increase the corrosion potential of SS316L by more than 410.57 mV and effectively reduced the corrosion current density by four orders of magnitude [16]. Lee et al. deposited Ti/TiN multilayers on SS316L via DC magnetron sputtering, showing better conductivity and corrosion resistance than single-layer TiN [17].

4.2 Electrical conductivity and contact resistance

Coatings also play a significant role in reducing interfacial contact resistance (ICR), which is critical for the efficient operation of fuel cells. The DOE target for ICR is less than 10 mΩ·cm^2, and achieving this is essential for maximizing the power output of the fuel cell [18]. Notably, the thermal expansion coefficients of TiN and titanium exhibit minimal differences (0.63 %), promoting enhanced adhesion between the TiN coating and the titanium bipolar plate. Furthermore, TiN demonstrates high electrical conductivity (4.55×10^6 S/m), establishing it as an ideal coating material for titanium bipolar plates [19, 20]. Jannat et al. [21] prepared Ti/TiN coatings on SS316L via PVD, achieving a corrosion current density of

0.095 μA/cm² in simulated PEMFC cathode environments, with ICR values of 11 mΩ·cm² (pre-polarization) and 18 mΩ·cm² (post-polarization), suitable for BPs.

4.3 Long-term stability and wear resistance

Performance Metrics: Recent studies have shown that coated metallic bipolar plates can achieve corrosion currents significantly below the DOE target, with many coatings demonstrating corrosion potentials between 400 mV and 550 mV vs. SHE. This indicates a strong performance in harsh operational environments [18]. Cheng et al. [22] performed a comprehensive study on the mechanical and tribological behavior of TiN/Ti multilayer coatings. Multilayers with a fixed TiN layer thickness and different Ti layer thicknesses were deposited by using a filtered arc deposition technique. The results revealed that increasing the Ti layer thickness from 0 to 150 nm lowered the hardness (from 32 to 16 GPa) and wear resistance, significantly. Su and Kao [23] performed an optimization study on multilayers with TiN/Ti/TiN and TiN/TiCN/TiN sequences. Experimental results indicated that a coating with a total thickness of 7 μm and layer sequence of TiN/TiCN/TiN exhibited good wear resistance. The potential of TiN/TiCN sequence for friction and wear reduction was further investigated by Zheng et al [24]. A maximum hardness and minimum wear rate of 34 GPa and 1.15 × 10−9 mm3/(N·mm), respectively, were obtained. The TiN/Ti/TiN sequence, despite a higher hardness value, showed a lower wear resistance. A minimum wear rate and COF of ~2×10−9 mm3/(N·mm) and ~0.6 (counterpart: 6 mm Al_2O_3 ceramic ball; load:1 N), respectively, were achieved. By adding a DLC layer on the top and reversing the deposition sequence of TiN and Ti (Ti/TiN/DLC), Liu et al. [18] tried to improve the friction and wear behavior of steel substrates. A minimum wear rate of approximately 1.2 × 10−9 mm3/(N·mm) under 5 N was obtained. The multilayer coatings showed maximum hardness values of 32 GPa and 20 GPa and the minimum COF values of 0.25 and 0.15, respectively (counterparts: 4mm steel ball and 6 mm Al_2O_3 ceramic ball). Notably, at the typical cathode potential of PEMFCs, Ti/TiN coatings show lower corrosion current densities than SS316L [25].
The development and evaluation of coatings for bipolar plates are critical for advancing fuel cell technology. By improving corrosion resistance and electrical conductivity, these coatings enhance the overall performance and durability of PEMFCs, making them more viable for commercial applications. Ongoing research continues to explore new materials and coating techniques to further optimize bipolar plate performance [12].

5. CHALLENGES AND LIMITATIONS ASSOCIATED WITH TI/TIN/DLC COATINGS IN PEMFC BIPOLAR PLATES

The application of Ti/TiN/DLC coatings on bipolar plates (BPs) in Proton Exchange Membrane Fuel Cells (PEMFCs) offers a promising solution to enhance corrosion resistance, electrical conductivity, and durability. However, several critical challenges remain in terms of cost, scalability, adhesion, performance degradation, long-term degradation mechanisms, and balancing coating properties with overall fuel cell performance.

5.1 Cost of Ti/TiN/DLC coatings and scalability issues

The cost of Ti/TiN/DLC coatings remains a significant barrier to the widespread adoption of metallic bipolar plates in PEMFCs. Although metallic materials like titanium and stainless-steel offer advantages in strength and conductivity, their high cost of processing, particularly for coated plates, impacts the overall cost-effectiveness of PEMFCs [18, 26]. Coating processes such as Physical Vapor Deposition (PVD) for TiN and Plasma Enhanced Chemical Vapor Deposition (PECVD) for DLC are expensive due to the need for specialized equipment and control of deposition parameters. Miyazawa et al. [27] studied the power performance of a single fuel cell with 316L stainless steel bipolar plates on the anode side. Their experimental results showed that after 300 h of testing, the degradation in cell performance was attributed to an increase in contact resistance between the bipolar plate and the gas diffusion layer (GDL). This was linked to a rise in the iron oxide (Fe ions) content in the passive film on the surface of the bipolar plates, as well as the precipitation of iron oxide downstream in the gas flow [28]. Scalability is another critical challenge, particularly for the DLC coatings, which require precise control over parameters like deposition power and precursor gas composition [29]. Achieving uniform coatings over large surface areas, especially at the high throughput required for commercial production, is a major hurdle. Despite advances in techniques like PVD and PECVD, these methods are not always economically feasible for mass production, particularly in terms of ensuring consistent coating quality across the large volume of bipolar plates needed for PEMFC stacks.

5.2 Adhesion problems and coating delamination

Adhesion of TiN and DLC coatings to the substrate is a fundamental issue that directly impacts the longevity and performance of PEMFCs. Both TiN and DLC coatings need to adhere strongly to the titanium or stainless-steel substrates to maintain their protective and conductive properties [30]. Poor adhesion can result in delamination, especially under the high mechanical stresses and thermal cycling experienced by bipolar plates during fuel cell operation. DLC coatings, in particular, are prone to high residual stresses, which can lead to cracking and delamination over time [31]. This issue is exacerbated when the coating thickness is increased, as thicker DLC coatings are more susceptible to stress-induced failure. Similarly, TiN coatings, while beneficial for corrosion resistance, can also suffer from adhesion failure if the deposition process or surface preparation is not properly optimized [32]. Enhancing adhesion through surface treatments such as plasma activation or improving the bonding between the coating and the substrate is an ongoing challenge.

5.3 Performance degradation due to high operational temperatures and humidity

Bipolar plates are essential components in PEMWE systems, playing a key role in conducting heat and electricity, enabling gas and water circulation, and providing mechanical support for the entire stack [33]. They represent approximately 48%–51% of the total system cost. The anode side of the bipolar plate faces harsh conditions during PEMWE operation, including high temperatures (60–80°C), strong acidic environments (pH 2–4), and high potentials (1.6–2.0 V). As a result, bipolar plates must exhibit exceptional corrosion resistance, electrical conductivity, and mechanical strength [34]. Titanium is frequently chosen as the substrate material for bipolar plates due to its low resistivity, high thermal conductivity, low permeability, and excellent strength. However, the titanium oxide passivation layer formed on the surface is less conductive, leading to increased ohmic resistance between the bipolar plate and the porous transport layer (PTL), which in turn reduces stack efficiency [35]. PEMFCs operate under conditions of elevated temperatures and humidity, which pose significant challenges to the durability of Ti/TiN/DLC-coated bipolar plates. The high temperature in the fuel cell environment accelerates the degradation of coatings, particularly for DLC, which can suffer from oxidation or loss of structural integrity at temperatures above 300°C. Similarly, the high humidity levels can lead to corrosion of the substrate beneath the coating if the coating itself is compromised, as the moisture may infiltrate micro-cracks or delamination sites. Ahmad et al. [6] investigated the use of titanium foam, prepared from pure titanium, in the production of bipolar plates for PEMFCs. Their study examined factors such as composition, sintering temperature, heating rate, and soaking time to optimize electrical conductivity, which was found to be 336.227 ± 240.61 S/cm using the Taguchi method [6]. Soma et al. [7] also utilized titanium as a bipolar plate material under simulated PEFC conditions. They observed high charge transfer and contact resistance at a cathode potential of 0.64 V, while the opposite was true at an anode potential of -0.36 V. TiN coatings, while providing excellent corrosion resistance, can also experience performance degradation under extreme conditions, such as high temperature and acidic environments. The formation of TiO_2 or other secondary phases due to oxidation at high temperatures can reduce the effectiveness of TiN coating, maintaining the stability of these coatings in the long term under operational conditions remains a major challenge.

5.4 Long-term degradation mechanisms

Long-term degradation mechanisms in Proton Exchange Membrane Fuel Cells (PEMFCs) are critical to understanding their durability and performance over extended operation periods [36]. These degradation processes are primarily driven by the harsh operating conditions, including high temperature, high humidity, and acidic environments. One key aspect of degradation is the material failure of bipolar plates, which are essential components that facilitate gas and water flow, provide electrical conductivity, and support the mechanical structure of the fuel cell stack [37]. A significant factor contributing to long-term degradation is the increased contact resistance between the bipolar plates and the porous transport layer (PTL). This increase in resistance is often due to surface oxidation, corrosion, and the growth of insulating oxide layers on the bipolar plates. For example, TiN-coated stainless steel (SS304) bipolar plates have shown significant improvement in performance over uncoated stainless steel by reducing corrosion rates and contact resistance [38]. However, even TiN coatings experience degradation under long-term exposure to acidic environments in PEMFCs. Over prolonged periods (e.g., 3000 h), the TiN coating gradually degrades, leading to the exposure of the underlying stainless steel, which increases the through-plane and contact resistance, thus reducing the efficiency of the fuel cell. Moreover, surface morphology changes, such as the formation of corrosion pits or the peeling off of the TiN layer, are observed after extended testing. These changes affect the hydrophobicity of the plates, further contributing to water management issues such as flooding, which negatively impacts cell performance. Corrosion also increases the roughness of the plate surface, exacerbating contact resistance [39]. As the surface roughens, the interfacial resistance between the bipolar plate and PTL becomes more significant, leading to a decline in the overall fuel cell efficiency. In the case of TiN-coated stainless steel bipolar plates, long-term degradation was quantified by monitoring changes in resistance over extended periods of operation [40]. The results show that while the TiN coating initially offers substantial protection against corrosion and significantly reduces contact resistance, its efficacy decreases over time due to the gradual delamination of the TiN layer, exposing the underlying stainless steel. This exposure allows for the oxidation of the stainless steel, further increasing resistance and contributing to the degradation of the fuel cell's performance. In general, while coatings like TiN can improve the longevity and efficiency of PEMFCs, their long-term performance is still affected by material degradation mechanisms such as oxidation, corrosion, and increased contact resistance [41]. Future improvements will need to focus on enhancing the durability of these coatings and minimizing the effects of long-term exposure to the harsh operating conditions of PEMFCs.

5.5 Trade-offs Between coating properties and fuel cell performance

In the context of PEMFCs, trade-offs between coating properties and fuel cell performance are a significant challenge, particularly when selecting materials for BPs. Bipolar plates play a central role in the operation of PEMFCs by providing electrical conductivity, distributing gases (hydrogen and oxygen), managing water, and ensuring structural integrity [42]. However, the material properties required for BPs often conflict, and trade-offs to optimize overall fuel cell performance. One of the major trade-offs occurs between corrosion resistance and conductivity [43]. Materials that offer high corrosion resistance, such as titanium-based alloys, are less prone to degradation under the harsh conditions in PEMFCs. However, these materials often have lower electrical conductivity compared to metals like stainless steel or graphite. For example, titanium alloys, although corrosion-resistant, suffer from higher resistance due to the formation of an insulating oxide layer on their surface, which impedes the efficient flow of electricity [44]. On the other hand, materials like stainless steel offer better electrical conductivity but are more vulnerable to corrosion under PEMFC operating conditions, which often include low pH environments and exposure to hydrofluoric acid (HF). This corrosion can lead to the dissolution of metal ions, which adversely affects the membrane's proton conductivity and can accelerate the degradation of the PEMFC stack [45].

Manufacturing and weight considerations also introduce trade-offs. For instance, while graphite-based BPs have good electrical and thermal conductivity, they are brittle and require costly machining processes for production, limiting their suitability for high-volume manufacturing [46]. In contrast, metal-based BPs can be mass-produced using methods like stamping or hydroforming, which are more cost-effective but come with challenges related to corrosion resistance. Furthermore, the weight of the bipolar plates is crucial for applications like automotive fuel cells, where reducing weight is essential. However, using lightweight materials often requires compromising on mechanical strength, as seen with certain metal alloys that, despite their low density, may not possess sufficient strength for long-term durability. Ultimately, the selection of materials for bipolar plates involves balancing cost, durability, corrosion resistance, conductivity, and mechanical properties to meet the demanding performance standards set by organizations like the US Department of Energy (DOE). Materials need to be durable enough to withstand the corrosive environment of PEMFCs while maintaining optimal conductivity and mechanical strength without significantly increasing the cost of production [12].

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