Improvement of platinum adhesion to carbon surfaces using PVD coatings

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Abstract

The adhesion of Pt to carbon surfaces is an important technological consideration in proton exchange membrane fuel cells (PEMFCs). Thin films of Au, Ti and Cr were deposited on graphite, non-hydrogenated diamond-like carbon (NH-DLC) and hydrogenated DLC (H-DLC) coatings' surfaces using a physical vapour deposition (PVD) process. The friction force curves obtained from sliding a Pt pin against these surfaces were used to evaluate the adhesion of Pt to the coated carbon surfaces. Interface strength calculations for graphite and diamond surfaces were carried out using first principles simulations. The incorporation of the interfacial PVD films enhanced the adhesion between Pt and graphite; rather than interfacial separation taking place, the bonds in graphite were broken (graphite decohesion) as confirmed by the first principles calculations. The bond between Pt and NH-DLC was stronger than that between Pt and graphite, and the transfer of Pt to the uncoated NH-DLC, as well as the Ti- and Cr-coated NH-DLC surfaces occurred as a result of the breaking of Pt–Pt bonds (Pt decohesion). Au film was peeled off the NH-DLC surface by the Pt pin contact, consistent with the calculated work of separation for the Au/carbon interface, which was weaker than works of decohesion for both NH-DLC and Pt. In case of the H-DLC, the low adhesion of Pt to this surface was improved by the PVD coatings, but the improvement was less compared to the coated graphite surfaces, as all PVD films were peeled off the H-DLC surfaces by the sliding action of the Pt pin.

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1. Introduction

A broad range of friction and adhesion properties are expected between carbon surfaces and metallic materials, as carbon forms different crystalline (e.g., graphite, diamond) and amorphous (e.g., diamond-like carbon (DLC)) structures, and these structures interact with the counterface and the surrounding environment in different ways.

The early works of Bowden and Young [1] showed that the friction of graphite and diamond surfaces was affected by the surrounding atmosphere, and the presence of surface films significantly reduced the friction. Other researchers [2–4] reported that if graphite is transferred to a metal’s surface during sliding in air a low friction between the metal and the graphite is obtained due to graphene layers (graphene planes) sliding over one-another. Recent studies that used first principles calculations [5–9] to model interfaces between metals and carbon structures proved to be useful for understanding the adhesion between metals and various types of carbon surfaces. For example, a first principles study of the adhesion of Al to graphite [5] demonstrated that the bonding between the graphite layers was weaker than the Al–C bond. Therefore, both surface conditions and subsurface properties may influence the adhesion of metals to graphite.

While graphite consists of sp² and diamond consists of sp³ bonds, a mixture of sp³/sp² bonds in the structure of DLC coatings gives intermediate characteristics to these materials. Consequently, DLC coatings’ properties strongly depend on the ratio of the sp³/sp² carbon bonds and the hydrogen content [10,11]. The incorporation of hydrogen into the DLC structure can effectively passivate the dangling carbon bonds at the surface. As a result, hydrogenated DLC (H-DLC) coatings display lower friction and less adhesion to the metallic surfaces than non-hydrogenated DLC (NH-DLC) coatings, suggesting that H-DLC coatings are generally more effective for mitigating Al adhesion, especially under inert atmospheres or under vacuum [6,12].

A combination of the aforementioned factors makes the adhesive characteristics of these carbon surfaces to metals complicated and difficult to predict or control. One of the most important examples of such challenges can be found in using carbon–supported Pt in proton exchange membrane fuel cells (PEMFCs). PEMFCs convert chemical energy to electrical energy by producing water vapour from hydrogen and oxygen. Both the oxidation of fuel (hydrogen or methanol) and the reduction of oxygen in a PEMFC need an electrocatalyst to proceed at reasonable rates. The dispersion of Pt particles on the carbon support is one of the main degradation mechanisms of the carbon-supported Pt catalyst [13], but the migration of Pt particles on the carbon support is one of the main degradation mechanisms of the carbon-supported Pt catalyst [14]. Modification of either the Pt catalyst or the carbon support has been suggested to increase the adhesion [15–18].

The substrate selection for this and other applications that require good adhesion between Pt and carbon surfaces is normally made on
an empirical basis. Yet, there is a need to understand how Pt interacts with carbon surfaces at a fundamental level. Thus, the purpose of this study was to understand the adhesion mechanisms that occur at the Pt/C interfaces during contact, and also to assess whether Pt adhesion to carbon surfaces could be improved with the implementation of thin metallic coatings. This was experimentally done by selecting three types of carbon surfaces, namely graphite, NH-DLC and H-DLC. The modification of the carbon surfaces with thin metallic layers is expected to improve the adhesion against Pt. For this purpose, a physical vapour deposition (PVD) process was used [19–21]. Au, Ti and Cr were deposited as thin layers on the carbon surfaces. The selection of the modifying metals was based on their chemical properties. Au is a noble metal, similar to Pt, and Ti and Cr are strong carbide-formers, likely to form strong bonds to carbon. A micro-scratch test was conducted to evaluate the adhesion between Pt and the modified carbon surfaces, and first principles simulations were carried out to determine the surface interactions at the atomic level.

2. Methodology

2.1. Experimental procedures

The graphite used as a substrate in this study was obtained in the form of a 3.18 mm thick plate with a high purity of 99.999%. The plate was cut into small pieces of $10 \times 10$ mm$^2$, which were then polished with a grit 1200 grinding paper wet with ethanol to obtain a surface roughness of $150 \pm 2$ nm. Graphit-iC™ and Dymon-iC™ DLC coatings with a thickness of $1.9 \pm 0.1$ μm and surface roughness values of $17 \pm 1$ nm and $11 \pm 1$ nm were also used as substrates (on which metallic layers were deposited). The DLC coatings, received from Teer Coatings Ltd. (Worcestershire, UK), had been deposited on hardened ($60 \pm 2$ Rockwell C) M2 steel discs from carbon and Cr (to enhance adhesion to the steel substrate) targets using an unbalanced magnetron sputtering system. Graphit-iC™ DLC is a hard (15–25 GPa) amorphous carbon coating with sp$^2$ bonding. Dymon-iC™ DLC is an amorphous, hydrogenated carbon coating (hydrogen content of about 40 at.% is achieved using a hydrocarbon gas precursor) with a high ratio of sp$^3$/sp$^2$ bonds and a lower hardness (12–18 GPa) [22,23].

Au, Ti and Cr were deposited as thin layers (~4 nm) on the graphite and DLC substrates, using an Edwards Auto 306 Magnetron Sputtering system. For each experiment, a vacuum of about 10$^{-3}$ Pa was reached before argon was injected into the chamber. An argon pressure of 0.8 Pa was reached and maintained throughout the sputtering process. The deposited films were not expected to change the roughness of the carbon surfaces, due to the very low thickness of the films.

A micro-scratch test was used to evaluate the adhesion strength between Pt and the modified carbon surfaces by determining the static friction force (F$_s$) [24]. A Pt pin was fabricated by mounting a 2 mm long Pt wire with a diameter of 1 mm lengthwise to the end of a steel rod. The configuration used in the scratch tests is schematically illustrated in Fig. 1a. The friction between the Pt pin and the uncoated and coated carbon surfaces was measured using a CSM micro-scratch system. The tangential friction force (F$_t$ in Fig. 1a) was recorded while running the tests at a constant normal load (F$_n$ in Fig. 1a) of 300 mN and a sliding speed of 33 μm/s for a total distance of 1 mm. The normal load was selected based on the sliding pair’s configuration and properties. Loads above 300 mN caused excessive indentation damage on the carbon surfaces. Loads lower than 300 mN generated friction forces that were too small to be accurately measured by the instrument. The sliding parameters used did not produce any significant increase in temperature [25]. As the temperature should reach 300 °C for thermal degradation of DLC surfaces to occur [26], the DLC surfaces were considered to remain stable during the micro-scratch tests.

![Fig. 1. (a) Schematic illustration of the configuration used in the micro-scratch tests. (b) Variations of the friction force with sliding distance for the graphite surfaces.](image-url)

The typical variations in friction force with sliding distance for the uncoated graphite, as well as the coated graphite surfaces are shown in Fig. 1b. F$_s$ is the maximum value of F$_t$ at the start of sliding, and it represents the tangential force required to break the initial bond between the surfaces in contact. The average value of F$_s$ was determined for each of the carbon surfaces in contact with the Pt pin, and it was used to evaluate the adhesion of these surfaces to Pt. The scratch marks on the carbon surfaces were studied using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) techniques. The purpose of these experiments was to investigate the peeling-off of the metallic films or the Pt transfer to the films.

2.2. First principles calculations

First principles simulations were carried out in order to understand the adhesion of Pt to graphite, NH-DLC and H-DLC at the atomic level. The calculations were carried out using a projector augmented-wave (PAW) method with exchange correlation energy approximated in the generalized gradient approximation (GGA) [27] to density functional theory (DFT), as implemented in the Vienna Ab initio Simulation Package (VASP) [28,29], where PAW-PBE [30,31] potentials were used as supplied by the VASP. 500 eV kinetic energy cut-off and $10 \times 10 \times 1$ grid of Γ-centered k-points were used to obtain 1–2 meV/atom convergence in total energies. The Pt surface was represented by a (111) plane; the graphite surface was represented by a single layer of graphite (0001); and the NH-DLC surface was represented by a clean diamond (111) plane. For the H-DLC, an H-terminated diamond surface was used. High resolution transmission electron microscopy (HRTEM) investigations [32,33] suggested that the interface between Pt catalyst...
and different types of carbon support prepared for the PEMFC electrodes were composed of the Pt (111) and graphite (0001) planes. Thus, the Pt pin/graphite plate interface in this study was represented by the Pt (111) and graphite (0001). A single metallic monolayer (Au, Ti or Cr) was inserted at the interfaces. The strength of the interfaces with a metal monolayer was determined by calculating the work of separation, $W_{\text{sep}}$, which is the energy required to reversibly separate an interface into two free surfaces [34]. The $W_{\text{sep}}$ was defined as:

$$W_{\text{sep}} = \sigma_1 + \sigma_2 - \sigma_{12} = \left( E_{\text{tot}}^1 + E_{\text{tot}}^2 - E_{\text{tot}}^{12} \right) / A$$

where $\sigma_1$ and $\sigma_2$ are the surface energies of slabs 1 and 2, $\sigma_{12}$ is the interface energy, $E_{\text{tot}}^1$ and $E_{\text{tot}}^2$ are the total energies of the slabs 1 and 2, $E_{\text{tot}}^{12}$ is the total energy of the interface constructed using slabs 1 and 2, and $A$ is the interface area.

3. Results and discussion

3.1. Experimental results

The average static friction forces between the Pt pin and the carbon surfaces coated with Au, Ti or Cr, compared to the uncoated surfaces are plotted in Fig. 2. Among the uncoated surfaces, the NH-DLC surface showed the highest adhesion to Pt, with a static friction force that was about three times of those measured for the other surfaces. While the PVD coatings improved the adhesion of Pt to the graphite and H-DLC surfaces, they had a reverse effect in the case of the NH-DLC surface. For graphite, all coatings similarly increased the adhesion to Pt, but they had different effects on the coated DLC surfaces, with Au generating the lowest adhesion and Cr the highest.

![Fig. 2. Average static friction forces between the Pt pin and the carbon surfaces coated with Au, Ti or Cr, compared with the same surfaces without any coatings. The static friction forces measured between the Pt pin and the PVD targets used to produce the thin films are presented as dash lines.](image)

![Fig. 3. SEM micrographs of the graphite contact surfaces with the Pt pin. Prior to the micro-scratch test, the graphite surfaces were: (a) uncoated; (b) Au-coated; (c) Ti-coated; and (d) Cr-coated. All micrographs are backscattered electron images except for (a).](image)
Fig. 2 also shows the static friction forces measured between the Pt pin and the PVD targets used to produce the thin films (dash lines in Fig. 2). All three lines (Pt/Au, Pt/Ti and Pt/Cr) are located higher than the entire friction force curves of graphite and H-DLC. This infers that for the coated graphite and H-DLC surfaces, the bonds that formed between Pt and the PVD films could be stronger than the bonds between the PVD films and the graphite or H-DLC surfaces.

SEM micrographs of the graphite’s contact surfaces with the Pt pin are shown in Fig. 3. No Pt particle could be detected on the contact surfaces of the uncoated or coated graphite. In case of the coated graphite surfaces, while the pin removed the coatings for the most part, small traces of Au, Ti or Cr could be detected by EDS on the contact surfaces, but with different morphologies (Fig. 3a–d).

SEM micrographs of the NH-DLC’s contact surfaces after sliding against the Pt pin are shown in Fig. 4. The uncoated NH-DLC contact surface was covered with a large number of micron-size Pt particles (Fig. 4a), a phenomenon that was not observed on the graphite or H-DLC surfaces. Among the films deposited on NH-DLC, only Au was peeled off by the Pt pin (Fig. 4b), and no trace of Pt could be detected on the NH-DLC surface. In contrast, the Ti and Cr thin films seemed to be mostly intact after sliding contact, but a few micro-scratches were observed on these coatings. Micron-size Pt particles were detected on the contact surfaces of the Ti- and Cr-coated NH-DLC surfaces, similar to the uncoated NH-DLC except that they were scarce, particularly in the case of the Ti-coated surface. The amount of the transferred Pt on the contact surfaces of the uncoated and the Ti- and Cr-coated NH-DLC surfaces correlated well with the static friction forces of these surfaces presented in Fig. 2, where the uncoated NH-DLC showed the highest adhesion to the Pt pin.

3.2. First principles calculations

In the presence of a metallic layer, the interface can be separated into two distinct surfaces—between Pt and the metallic layer (Pt–X), and between carbon and the metallic layer (C–X). The $W_{\text{sep}}$ of both of these bonds was computed for all interfaces, and they were compared to the works of decohesion ($W_{\text{dec}}$) of the bulk materials (i.e., Pt, graphite and diamond), as illustrated in Fig. 5. In this figure, $W_{\text{sep}}$ for breaking the interface at the Pt–X bond ($W_{\text{sep}}^{\text{Pt-X}}$) and the C–X bond ($W_{\text{sep}}^{\text{C-X}}$) is shown for each of the metallic coatings. The Pt/graphite interface has a $W_{\text{sep}}$ of 0.01 J/m² that is lower than $W_{\text{dec}}$ of both graphite (0.08 J/m² [5]) and Pt (2.91 J/m²). Fig. 5a shows that at the Pt/graphite interfaces coated with the metallic films, $W_{\text{sep}}^{\text{graphite}}$ is lower than $W_{\text{sep}}^{\text{Pt-X}}$ and $W_{\text{dec}}^{\text{Pt}}$, so during sliding, the Pt/graphite interface is expected to break from the bulk graphite. Therefore, the incorporation of the interfacial metallic layers enhanced the adhesion between Pt and graphite. In case of the Au-coated graphite, however, a mixed interfacial failure mechanism may occur, because the values of $W_{\text{sep}}^{\text{C-X}}$ and $W_{\text{dec}}^{\text{graphite}}$ are very close (Fig. 5a). These predictions are in good agreement with the experimental observations, where all coated graphite surfaces showed higher friction forces against the Pt pin (Fig. 2).

Fig. 5b shows that at the Pt/diamond interface, the incorporation of Ti and Cr layers increased the interfacial strength compared to the pure Pt/diamond interface, which has a $W_{\text{sep}}$ of 3.62 J/m². The calculated $W_{\text{dec}}$ (2.91 J/m²) was less than $W_{\text{sep}}^{\text{Pt-C}}$, as well as $W_{\text{sep}}^{\text{Pt-X}}$ and $W_{\text{sep}}^{\text{C-X}}$ for both Ti and Cr. Therefore, shearing the Pt/diamond interface is expected to prompt a fracture in the bulk Pt for the uncoated as well as the Ti- and Cr-coated diamond surfaces. Consequently, when

![Fig. 4. SEM micrographs of the NH-DLC contact surfaces with the Pt pin. Prior to the micro-scratch test, the NH-DLC surfaces were: (a) uncoated; (b) Au-coated; (c) Ti-coated; and (d) Cr-coated. All micrographs are secondary electron images.](image-url)
Pt is sliding against these surfaces, the transfer of Pt to the NH-DLC surfaces is expected to occur (Fig. 4a, c and d). On the other hand, when the diamond surface is coated with Au, the C–X interface becomes the weakest, with a $W_{\text{sep}}^{C-X}$ of 1.93 J/m². As a result, in the sliding experiments between Au-coated NH-DLC and Pt, the transfer of Au to the Pt surface is expected (Fig. 4b).

The calculations for the interfaces between Pt and an H-terminated diamond surface modified with the metallic layers showed very low adhesions between carbon and the metallic species ($W_{\text{sep}}^{C-X} = 0.15$ J/m²), due to the passivation of the carbon dangling bonds at the diamond surface by hydrogen [6]. Therefore, when Pt is sliding against H-DLC, transfer of the metallic films (i.e. Au, Ti and Cr) to the Pt surface is expected (Fig. 6).

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Graphite</th>
<th>NH-DLC</th>
<th>H-DLC</th>
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<tbody>
<tr>
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<td></td>
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<tr>
<td>No Pt transfer</td>
<td></td>
<td>Pt transfer to NH-DLC</td>
<td>No Pt transfer</td>
</tr>
<tr>
<td>Weakest Bond</td>
<td>Pt-C</td>
<td>Pt-Pt</td>
<td>Pt-H</td>
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<tr>
<td>Au Coating</td>
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<tr>
<td>Au transfer to Pt</td>
<td>C-Au / C-C</td>
<td>C-Au</td>
<td>Au transfer to Pt</td>
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<td>Weakest Bond</td>
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<td>Ti Coating</td>
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<td>Ti and C transfer to Pt</td>
<td>Pt transfer to NH-DLC</td>
<td>Ti transfer to Pt</td>
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<td>Weakest Bond</td>
<td>C-C</td>
<td>Pt-Pt</td>
<td>Ti-H</td>
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<td>Cr Coating</td>
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<td>Cr and C transfer to Pt</td>
<td>Pt transfer to NH-DLC</td>
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<tr>
<td>Weakest Bond</td>
<td>C-C</td>
<td>Pt-Pt</td>
<td>Cr-H</td>
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Fig. 5. The adhesion strength of Pt against: (a) graphite and (b) diamond. The adhesion strength was characterized by the work of separation.

Fig. 6. SEM micrographs of the Pt pin scratch marks on graphite, NH-DLC and H-DLC surfaces, coated with thin films of Au, Ti and Cr. Sliding directions in all micrographs were from right to left, and the scratch marks are approximately 1 mm long. The weakest interfacial bond was calculated using first principles calculations (see Section 2.2).
3.3. Summary of experimental and computational results

Fig. 6 provides a summary of the experimental observations and computational results. SEM micrographs of the scratch marks made by the Pt pin on all uncoated and PVD-coated carbon surfaces and the transferred material for each case (experimentally observed), have been presented together with the weakest bond calculated by first principles simulations. The experimental results are in a good agreement with the computational results. The main results can be summarized in the following way:

i) Among the uncoated carbon surfaces, NH-DLC showed the strongest adhesion to Pt, while the adhesion of graphite to Pt was weaker, with H-DLC being the weakest.

ii) Incorporation of the Au, Ti and Cr interfacial films enhanced the adhesion between Pt and graphite, resulting in the graphite decohesion (i.e., breaking of the bonds between the graphite layers) rather than interfacial separation, as confirmed by the first principles calculations.

iii) The strong bond between NH-DLC surfaces and Pt resulted in Pt decohesion (i.e., breaking of the Pt–Pt bonds) and transfer of Pt to the uncoated NH-DLC, as well as the Ti- and Cr-coated NH-DLC surfaces. Au film was peeled off from the NH-DLC surface by the Pt pin in contact, consistent with the calculated $W_{\text{sep}}$ of the Au/C interface, which was smaller than $W_{\text{deg}}$ of both diamond (NH-DLC) and Pt.

iv) The metallic coatings slightly improved the adhesion of Pt to the H-DLC surfaces, but they were all peeled off by the Pt pin during the scratch test, a result that was also consistent with first principles calculations.

Therefore, Pt adhesion to graphite can be improved by the application of interfacial thin layers of Au, Ti or Cr. This may be used to enhance the Pt catalyst durability in PEMFCs. However, these metallic films are not likely to further improve the already strong adhesion of Pt to NH-DLC substrates.

4. Conclusions

Thin films of Au, Ti and Cr were deposited as thin layers on graphite, non-hydrogenated diamond-like carbon (NH-DLC) and hydrogenated DLC (H-DLC), using an RF magnetron sputtering system, with the purpose of studying the adhesion mechanisms and improving the adhesion of Pt to these surfaces. It was concluded that the metallic films improved the adhesion of Pt to graphite, whereas the adhesion of Pt to NH-DLC was strong enough without the application of these thin films.

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