Emerging Layered Materials and Their Applications in the Corrosion Protection of Metals and Alloys

Ramaraj Sukanya 1, Tara N. Barwa 1, Yiran Luo 1, Eithne Dempsey 1,2 and Carmel B. Breslin 1,2,*

1 Department of Chemistry, Maynooth University, W23 F2H6 Maynooth, Co. Kildare, Ireland; sukanARAM33@GMAIL.COM (R.S.); tara.barwa.2023@Mumail.ie (T.N.B.); yiran.luo.2023@Mumail.ie (Y.L.); eithne.dempsey@mu.ie (E.D.)

2 Kathleen Lonsdale Institute for Human Health Research, Maynooth University, W23 F2H6 Maynooth, Co. Kildare, Ireland

* Correspondence: carmel.breslin@mu.ie

Abstract: Metals and alloys are essential in modern society, and are used in our daily activities. However, they are prone to corrosion, with the conversion of the metal/alloy to its more thermodynamically-favored oxide/hydroxide phase. These undesirable corrosion reactions can lead to the failure of metallic components. Consequently, corrosion-protective technologies are now more important than ever, as it is essential to reduce the waste of valuable resources. In this review, we consider the role of emerging 2D materials and layered materials in the development of a corrosion protection strategy. In particular, we focus on the materials beyond graphene, and consider the role of transition metal dichalcogenides, such as MoS2, MXenes, layered double hydroxides, hexagonal boron nitride and graphitic carbon nitride in the formulation of effective and protective films and coatings. Following a short introduction to the synthesis and exfoliation of the layered materials, their role in corrosion protection is described and discussed. Finally, we discuss the future applications of these 2D materials in corrosion protection.

Keywords: corrosion protection; corrosion inhibitors; layered double hydroxides; dichalcogenides; protective coatings; MXenes; molybdenum disulfide; hexagonal boron nitride; graphitic carbon nitride

1. Introduction

Metals and alloys are essential in modern society, and depending on their properties, they are used in a multitude of applications. For example, aluminum and titanium are lightweight and find applications in the aerospace industry [1], while copper or electroplated copper is typically employed in electronic applications [2], and steels are used in construction and transportation [3]. Although advances have been made in the processing of metals and alloys, leading to improvements in their performance, metals and alloys are prone to corrosion [4]. This is a natural process that converts the pure metal or alloy, when in contact with its environment, into its thermodynamically-favored oxide, hydroxide, carbonate or sulfide. As a result, there is gradual deterioration and destruction of the material, which can eventually lead to a loss in function, structural failure, or indeed environmental contamination with the release of hazardous metal ions. Additional metals or alloys are often employed to replace the failed component, and this has implications for sustainability with an over-utilization of natural resources [5]. Sustainability is an essential consideration in the modern world. Accordingly, innovative corrosion-protection strategies are required to minimize the premature repair or replacement of metals and alloys.

The corrosion reaction can be described as two half-cell reactions, as illustrated in Equations (1) and (2), or in Equations (1) and (3), where Me represents a metal or alloy in an aqueous media or with a layer of adsorbed water molecules, which is relevant in atmospheric corrosion. The conversion of Me to Me^{n+} corresponds to the oxidation half reaction, while the accompanying reduction half reaction may involve either the reduction...
of dissolved O\(_2(g)\), as seen in Equation (2), or the reduction of H\(^+\)(aq), which becomes the favored reaction under acidic conditions. As these reactions proceed, different forms of corrosion emerge, including more general dissolution, or localized forms of corrosion, such as pitting [4,6], crevice, intergranular or galvanic corrosion [7]. Another form that can traced to the environment in which Me functions includes stress corrosion [7].

\[
\text{Me} \rightarrow \text{Me}^{n+} + n\text{e}^- \quad (1)
\]

\[
\text{O}_2(g) + 4\text{H}^+(aq) + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}(aq) \quad (2)
\]

\[
2\text{H}^+(aq) + 2\text{e}^- \rightarrow \text{H}_2(g) \quad (3)
\]

In order to protect Me from corrosion, the transfer of electrons must be impeded or eliminated by inhibiting the oxidation half, reduction half or both half reactions. For many years, hexavalent chromium (Cr(VI)) was used as a very effective corrosion inhibitor [8], but with its high levels of toxicity to both humans and aquatic life, it is no longer an option in the design of corrosion-protective coatings or technologies [9]. Consequently, alternative approaches are required, and various surface modifications and protective coatings have been formulated, ranging from polymeric coatings [10,11] and conversion coatings [12] to the employment of more recent materials, such as metal organic frameworks (MOFs) [13], all aimed at preventing or reducing the rate of corrosion [14,15].

Since the discovery of graphene, a host of new 2D materials has been uncovered or rediscovered, and these materials, with their intriguing properties, are finding applications in different sectors, ranging from energy [16,17] and sensors [18] to biomedical applications [19]. It is no surprise that they are also emerging as suitable materials for the corrosion protection of metals and alloys. Among the various 2D materials that have attracted attention in the formulation of corrosion protection strategies, graphene is one of the most widely considered [20,21]. However, the long-term corrosion-protective capacity of graphene is not always satisfactory [22], and there are a number of good reviews already available in the literature that describe the performance and limitations of graphene in the development of a corrosion-control technology [23,24].

Accordingly, in this review, we focus on other families of emerging layered and 2D materials, and these include transition metal dichalcogenides (TMDs), layered hexagonal boron nitride (h-BN), graphitic carbon nitride (g-C\(_3\)N\(_4\)), MXenes and finally the more established layered double hydroxides (LDHs), as illustrated in Figure 1. Initially, we briefly introduce these materials and describe some of the most common methods employed in their synthesis. Next, we review and discuss the corrosion-protective properties of the selected 2D materials. Finally, the challenges that remain to be resolved before these 2D materials can be employed in the design of a corrosion protection technology are highlighted and discussed.
2. Layered Materials and Their Fabrication Methods

In Figure 2, schematic representations of layered LDHs [25], TMDs [26], MXenes [27], h-BN [28] and g-C₃N₄ [29] are presented. This highlights the layered assemblies that exist with different elements or combinations of elements. In these layered structures, van der Waals forces exist between the adjacent layers, and these control the interlayer distance and stacking modes. The LDHs (Figure 2A), are a family of ionic layered double hydroxides, and can be represented as \( \left[ M^{2+}_{1-x} M^{3+}_x (OH)_2 \right]^{q+} (A^{n-})^{q/n} \cdot yH_2O \), where M is a cation and A represents an anion [30]. The divalent cationic species are commonly Mg²⁺, Zn²⁺, Fe²⁺ or Ni²⁺, while the trivalent cations are typically Al³⁺ or Fe³⁺. Charge compensation of the divalent and trivalent cations is achieved with anions, Aⁿ⁻, and these can include CO₂⁻, Cl⁻, SO₄²⁻ and RCO₂⁻. Clearly, LDHs have interesting characteristics in terms of the formulation of a corrosion control technology, as corrosion inhibitors can be easily introduced as the A species [31]. In the literature, LDHs are normally represented as M-M-LDH (e.g., Mg-Al-LDH) and this notation is also used in this review.

The TMDs can be represented as MX₂, where M is a transition metal such as Mo or W, and X represents the chalcogen atoms, S, Se or Te [32]. The M atoms are sandwiched between two chalcogen atoms to give X–M–X. The most widely studied TMD is MoS₂, which is finding applications in a diverse range of sectors, including energy [33] and sensors [34]. The layers are stacked and held by weak van der Waals forces, as illustrated in Figure 2B, while covalent bonding exists between the M and X atoms. The TMDs can exhibit different crystal phases, with the two main phases being the octahedral coordination phase (1T), which exhibits metallic-like properties, and the trigonal prismatic phase (2H), which has semiconductor-like characteristics.

MXenes are another interesting family of 2D materials, and comprise metal carbides or nitrides [35,36]. These are derived from their parent MAX phase, which has a 3D structure, as illustrated in Figure 2C. The MAX phases are denoted as Mₙ₊₁AXₙ, where M represents an early transition element, such as Ti; A corresponds to a Group 13 or 14 element, usually Al; and X is carbon or nitrogen [35]. The n is an integer, and can adopt values ranging from 1 to 3. The MAX phases adopt a typical solid structure, but once the Al layer is etched and removed, the resulting layers are stacked in a hexagonal lattice, as shown in Figure 2C, where the characteristic accordion morphology is evident. The MXenes can be formed by the selective etching of the A element, as the bonding between M-A is generally weaker than between M-X [37].
In terms of scalability, large-scale manufacturing and relevance to corrosion protection technologies, the top-down approaches are more applicable. Although the epitaxy-based approaches are more applicable. Although the epitaxy-based approaches are more applicable. Although the epitaxy-based approaches are more applicable. Although the epitaxy-based approaches are more applicable. Although the epitaxy-based approaches are more applicable. Although the epitaxy-based approaches are more applicable. Although the epitaxy-based approaches are more applicable. Although the epitaxy-based approaches are more applicable. Although the epitaxy-based approaches are more applicable. Although the epitaxy-based approaches are more applicable. Although the epitaxy-based approaches are more applicable. Although the epitaxy-based approaches are more applicable. Although the epitaxy-based approaches are more applicable. Although the epitaxy-based approaches are more applicable. 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technologies, the top-down approaches are more applicable. Although the epitaxy-based methods can be employed to produce defect-free monolayers with high crystallinity, they are very sensitive to the substrates, and require specific orientations. The first step in the top-down approach is the production of the parent bulk material, which is then followed by an exfoliation step. The methodologies employed in the synthesis of the bulk materials are summarized in Table 1, where it is evident that the parent LDHs and TMDs are relatively easily formed using hydrothermal synthesis [47,48]. In contrast, g-C$_3$N$_4$ is formed through the pyrolysis of nitrogen-rich precursors [49]. High-temperature processing, and in many cases high pressures, are required in the preparation of bulk h-BN [50,51] and the MAX phases are formed by sintering processes [52].

Table 1. Summary of the main synthesis methods used to form the 2D materials.

| Methodology                              | Bulk Material  | Details                                                                 |
|-----------------------------------------|----------------|-------------------------------------------------------------------------|
| hydrothermal/solvothermal synthesis     | TMDs, LDHs     | Relatively low temperatures, 100–200 °C, short processing times, economic, and an environmentally acceptable water-based synthesis (hydrothermal). Addition of organic solvents (solvothermal) can be used to tune the properties of the final product, including shape and size. Overall, efficient, fast and simple approach. |
| co-precipitation solution-based reactions| LDHs           | Simple solution-based reactions, involving precursor salts of the LDH cations and anions, can be carried out at room temperature or at slightly elevated temperatures. |
| high temperatures and/or pressures      | h-BN           | Temperatures in the vicinity of 1300° to 1800 °C are employed.        |
| sintering methods                       | MAX phases     | Temperatures in the vicinity of 1100° to 1500 °C are employed.        |
| pyrolysis and polycondensation          | g-C$_3$N$_4$   | Pyrolysis of nitrogen-rich precursors, followed by polycondensation; requires temperatures in the vicinity of 550 °C. |

Once formed, the parent layered materials can be exfoliated, and liquid phase exfoliation (LPE) [53] is the more commonly employed routine. It involves the use of ultrasonication or high-shear mixing to effectively peel off layers, to produce single or a few stacked layers [53]. Another interesting exfoliation approach is based on the formation of intercalation compounds [54,55]. In this case, the intercalation compound is formed by the insertion of ions, atoms or molecules into the interlayer spacing of the bulk material. This, in turn, gives rise to an increase in the interlayer distance, weakening the van der Waals forces, making it easier to deliver the exfoliated sheets. Nevertheless, processing of the parent layered material to give 2D monolayers or a few layered sheets can vary greatly, depending on the materials. For example, the production of 2D MXenes normally involves etching of the Al layers, and this requires aggressive HF etching, or fluoride salts combined with HCl, to oxidize the Al and form AlF$_3^-$ in solution [37]. As illustrated in Equations (4)–(6), etching of the Ti$_3$AlC$_2$ MAX phase gives MXenes with –F and –OH terminal groups, Ti$_2$C$_3$F$_2$ or Ti$_2$C$_3$(OH)$_2$. The surface terminal groups depend on the composition of the etching solution, with the addition of HCl giving rise to –Cl terminal groups.

$$\text{Ti}_3\text{AlC}_2 + 3\text{HF} \rightleftharpoons \text{AlF}_3 + \text{Ti}_3\text{C}_2 + \frac{3}{2}\text{H}_2(g)$$  \hfill (4)  
$$\text{Ti}_3\text{C}_2 + 2\text{H}_2\text{O} \rightleftharpoons \text{Ti}_3\text{C}_2(\text{OH})_2 + \text{H}_2(g)$$ \hfill (5)  
$$\text{Ti}_3\text{C}_2 + 2\text{HF} \rightleftharpoons \text{Ti}_3\text{C}_2\text{F}_2 + \text{H}_2(g)$$ \hfill (6)
On the other hand, the liquid phase exfoliation of bulk MoS$_2$, g-C$_3$N$_4$, h-BN and LDHs can be achieved more readily, to produce a few atomic layers of nanoplatelets [56,57]. However, the electrostatic interactions and the interlayer hydrogen bonding between the LDH layers can make the exfoliation process in water-containing solvents complex, and it can be difficult to avoid the restacking of the layers. While LPE is used extensively in the formation of single and a few layered nanosheets, the yield, quality, size and size dispersion of the 2D sheets depend on the solvent, sonication time and energy, and can be difficult to control. The influence of the solvent system is evident in Figure 3, where it is clear that poly(2-butyl aniline) (PBA) can considerably enhance the dispersion of h-BN and its stability. On the other hand, the h-BN agglomerates following a 24 h storage period in the absence of PBA.

![Figure 3. Illustration showing the influence of PBA on the dispersion of h-BN in THF (left: h-BN in THF, right: h-BN in THF and PBA). Reprinted with permission from Cui et al. [38], copyright Elsevier, 2018.](image)

3. Coatings and Corrosion Protection

Corrosion-protective coatings have become the focus of considerable attention in a wide variety of applications [59], as they provide a barrier between the environment and the substrate metal or alloy. A number of very good reviews are available, describing the variety of coatings that have been employed, their roles in protecting metals and alloys in different environments and the events that lead to their loss of protection [60,61]. The ideal coating should provide an impermeable barrier to moisture and corrosive species, and exhibit long-term stability without cracking or delamination, which are the main failure mechanisms. In this regard, layered and 2D materials are interesting, as they can enhance barrier protection by impeding the diffusion of oxygen, water and corrosion-promoting ions, such as chloride anions. In theory, the impermeable nature of the 2D sheets can not only impede diffusion, but they can also be exploited to fill pores in the coatings, extending their protection period. In addition, smart coatings that can exhibit self-healing characteristics at defective sites, which would otherwise develop into corrosion sites, are especially interesting, and LDHs [62,63] and MXenes [64] can potentially serve as corrosion inhibitor nanocarriers.

In assessing and measuring the corrosion-protective efficiency of coatings, a number of experimental techniques and parameters can be employed, and these include corrosion current density ($j_{corr}$) and corrosion potential ($E_{corr}$) measurements, electrochemical impedance spectroscopy, salt spray tests, humid air environments and scratch tests. The $j_{corr}$ and $E_{corr}$ parameters provide useful information in the analysis of coatings, with $j_{corr}$ being a measure of the rate of the corrosion reaction and $E_{corr}$ representing a thermody-
namic factor. The Butler–Volmer equation (Equation (7)), can be applied to the corrosion reaction, which comprises both the anodic and cathodic electron transfer half reactions. In this analysis, \( E - E_{\text{corr}} \) corresponds to the overpotential, and \( \alpha_a \) and \( \alpha_c \) are the charge transfer coefficients for the anodic and cathodic reactions, respectively.

\[
j = j_{\text{corr}} \left( e^{\alpha_a F (E - E_{\text{corr}}) / RT} - e^{-\alpha_c F (E - E_{\text{corr}}) / RT} \right)
\]

A protective coating should ideally have a much lower \( j_{\text{corr}} \) value than the corresponding uncoated substrate. Depending on whether the coating impedes the reduction reaction or the oxidation half reaction, the \( E_{\text{corr}} \) value can shift in a negative or positive direction. When the anodic oxidation reaction is inhibited, a lower \( j_{\text{corr}} \) is observed, while \( E_{\text{corr}} \) adopts a more positive value. Similarly, if the rate of the reduction reaction is lowered, then \( E_{\text{corr}} \) is shifted to more negative values and \( j_{\text{corr}} \) decreases. This can be explained using mixed potential theory [21]. These parameters are normally obtained from slow scan polarization curves [65], while cyclic polarization curves can also be very useful in determining the re-passivation characteristics [66].

However, these analyses are not suitable for organic coatings with high ohmic resistances, as the potential drop across the polymer layer is much larger than that across the metal-polymer interface. Accordingly, electrochemical impedance spectroscopy is frequently employed in the analysis of high-resistance organic coatings [67]. This technique is especially useful as it can be employed to monitor water uptake, which normally alters the capacitance of the organic coating, while events such as corrosion at the polymer/metal interface and the formation of defects in the coating alter the impedance [67]. Impedance measurements are also employed in a wide range of coatings with lower resistances, such as LDHs [68]. The impedance data can be fitted to equivalent circuits, or the coating performance can be assessed by monitoring the impedance at low frequencies in the vicinity of 10 mHz [69].

Accelerated corrosion tests in humid air, humid air with gaseous contaminants and salt spray tests are commonly used to evaluate the performance of coatings [70]. The salt spray tests are typically carried out in a NaCl spray at slightly elevated temperatures. The integrity of the coating and the build-up of corrosion products are monitored as a function of time. Scratch tests are very useful when it comes to smart corrosion-inhibitor-releasing coatings [71]. A scratch is made in the protective coating, and the coating’s self-healing capacity can be assessed by monitoring the extent of corrosion at the created defect. The American Society for Testing Materials (ASTM) has developed a number of standard methods (for example, ASTM B117, which is a salt spray test) to evaluate localized and general corrosion, and these are very useful in assessing and comparing the corrosion-protective properties of new coatings.

While 2D materials are frequently used as fillers in organic and waterborne coatings [72], they have also been applied directly to the substrates [73]. Additionally, 2D materials with semiconducting properties can be employed in photocathodic protection [74,75]. These emerging layered materials have potential applications in the protection of metals and alloys in marine environments [76], in the protection of steel in concrete [77], as fillers in coatings for applications in transport and infrastructure (such as buildings and pipelines) and they can also serve to protect substrates at high temperatures [78]. In the following sections, each of the layered and 2D materials and their applications in the formulation of protective and anticorrosion coatings are described and reviewed.

### 3.1. Layered Double Hydroxides

Although LDHs can be exfoliated, it is normally the layered LDHs and not the 2D LDH nanosheets/nanoplatelets that are employed in the design of the current corrosion-protective coatings. Two main approaches have emerged: the LDHs can be synthesized and then applied to the corrosion-susceptible metal or alloy using for example spin coating [79], or an in situ approach is possible, especially with Al- and Mg-based systems [80]. It
is generally accepted that this in situ method, where the substrate provides the cations required for nucleation of the LDHs, is more promising due to the good adhesion between the substrate and the LDH.

As detailed in Table 1, LDHs can be conveniently fabricated using hydrothermal synthesis, where H$_2$O is employed as the solvent system. Typically, the LDH precursors are combined in solution and then autoclaved at relatively low temperatures, in the vicinity of 80$^\circ$ to 150$^\circ$C [81,82]. This methodology can be easily tailored to deposit the LDHs directly onto a metal or alloy substrate. For example, Hou et al. [80] formed a Mg-Al-LDH by placing the Mg substrate in an alkaline Al(NO$_3$)$_3$ solution, which was then transferred to an autoclave reactor and heated at 120 $^\circ$C for 12 h. This is an effective way of depositing adherent LDHs onto corrosion-susceptible substrates. It relies on the oxidation of the substrate during the hydrothermal process to produce the divalent or trivalent cations required to form the LDHs. It has been used to deposit LDHs directly onto Al and Mg and their alloys [80–83], as Al$^{3+}$ and Mg$^{2+}$ cations are generated in situ during the hydrothermal reaction. An adaption of this method was used by Zhang et al. [73] to fabricate a Mg-Fe-LDH on a Mg substrate. Initially, an amorphous FeOOH film was electrochemically deposited on the Mg substrate, and then the LDH was nucleated by hydrothermal treatment in pure water to produce the Mg-Fe-LDH. Alternatively, divalent and trivalent precursors can be combined in the solution phase, and employed to nucleate the LDH onto the substrate. This methodology was employed to nucleate Zn-Al-LDH onto a Mg alloy. In this case, Zn(NO$_3$)$_2$ and Al(NO$_3$)$_3$ salts, at a concentration ratio of 2:1, were combined with the Mg alloy and heated in an autoclave at 80 $^\circ$C for 12 h.

Due to the elevated temperatures employed in hydrothermal synthesis, LDHs with good crystallinity can be formed. In addition, other components, such as graphene oxide (GO) [84,85] and corrosion inhibitors [86], can be easily combined with the LDHs in a one-step hydrothermal experiment, as illustrated in Figure 4. Using this approach, Yan et al. [84] formed graphene-modified LDHs by dispersing GO with the Zn(NO$_3$)$_2$ and Al(NO$_3$)$_3$ precursor salt solution, while corrosion inhibitors, namely aspartate and laurate anions [86], were incorporated into the LDH in a single step. Clearly, hydrothermal synthesis exhibits high flexibility in terms of additives, morphology, crystal orientation, and structure of the final LDH. Nevertheless, the hydrothermal method requires temperatures elevated above room temperature and reaction times of several hours. Accordingly, the co-precipitation method is more widely employed.

Figure 4. Schematic representation of the preparation of aspartic acid intercalated LDH/rGO hybrids. Reproduced with permission from Zhong et al. [85], copyright Elsevier, 2019.
In co-precipitation, a wide range of interlayer anions, including various corrosion inhibitors, can be employed, and the synthesis is suitable for upscaling. Typically, hydrated chloride or nitrate salts are used, but also it is possible to form LDHs using oxide phases, such as MgO [77]. It has been shown that the crystallinity of the LDHs can be improved by using the hydrolysis of urea [79,87]. This slow and progressive hydrolysis reaction maintains an alkaline environment through the generation of carbonates, which then become the interlayer anions. Ferreira et al. [31] used the co-precipitation method to synthesize Zn-Al-LDH, to produce the precipitation of vanadate-loaded LDHs. These LDHs were subsequently dried and processed as powders, added to a commercial paint and used to protect AA2024. In this routine, Zn(NO$_3$)$_2$ and Al(NO$_3$)$_3$ were dissolved and combined with NaVO$_3$. The pH of the slurry was maintained constant at 9.5 by the addition of NaOH over a 90 min period at 25 $^\circ$C. Co-precipitation is also widely employed to produce the in situ deposition of LDHs, as this tends to provide good adhesion between the LDHs and the corrosion-susceptible substrates [88].

Although LDHs are more frequently deposited onto Al- and Mg-based substrates, they have been employed in the corrosion protection of copper and its alloys [89–91] and iron and steels [92–94]. In a recent report, Nikhil and Prakash [89] used the co-precipitation method to initially form the LDH, which was then placed with the copper substrate in an autoclave and subjected to the hydrothermal approach. This resulted in the deposition of the LDH onto the copper substrate. Similarly, Zuo et al. [94] formed a Mg-Fe-LDH protective film on a steel plate using the hydrothermal method. The steel was placed in the autoclave with a magnesium salt and urea to produce the in situ formation of the LDH on the steel substrate.

It is well known that the experimental conditions employed in both hydrothermal and co-precipitation synthesis can influence the properties of the fabricated LDHs [87]. Experimental parameters such as the concentration of reactants, pH, temperature and aging can all influence the particle size, morphology and crystallinity of LDHs, as illustrated in Figure 5, where the influence of pH is summarized. In general, the crystallinity is enhanced with increasing temperatures. In a recent study, LDH thin films were formed on AA6082 using the hydrothermal method, and the influence of temperature (from 40 to 100 $^\circ$C) and treatment time (from 12 to 24 h) were studied [82]. It was found that the LDH coating formed at 100 $^\circ$C for 18 h adopted a more dense and compact structure, and exhibited the highest corrosion-protective properties. In a related study, the same group found that the more corrosion-protective LDH coating was formed on AA6082 at a pH of 6.5 combined with a reaction time of 18 h at 80 $^\circ$C [95]. Likewise, Alibakhshi et al. [96] have shown that the interlayer spacing depends on the pH employed during co-precipitation. At high pH values in the vicinity of 11.5 to 12.5, a decrease in the interlayer spacing was observed, while at lower pH values of about 9.5 a higher amount of nitrate and a low carbonate content gave rise to a closer spacing between the layers. Interestingly, the higher interlayer spacings resulted in better corrosion inhibition, and this was attributed to a higher nitrate concentration (which acts as an inhibitor) and greater chloride entrapment. It is also very well known that carbonates are very difficult to remove from LDHs, and a nitrogen atmosphere to exclude CO$_2$ is required to prevent the incorporation of carbonate within LDHs [93]. These studies demonstrate the importance of experimental parameters in the formation of LDHs.
The corrosion-protective properties of LDHs are normally attributed to a barrier effect, coupled with their anion exchange capacity. These anion exchange characteristics can be exploited to provide the controlled release of corrosion inhibitors. By loading LDHs with appropriate corrosion inhibitors, a triggered protection mechanism can be initiated, whereby the inhibitors are released in response to some change, such as pH, at a developing corrosion site. As a result, the corrosion event is halted [97–99]. This has the potential to give long-term corrosion protection. Various corrosion inhibitors have been incorporated as the anionic species within LDHs, and these include inorganic compounds such as molybdate [100–103], permanganate [104], nitrate [105–107], nitrite [77,108,109], phosphate [62], phenylphosphonate [110] and vanadate [111–113]. Also, organic inhibitors such as benzoate, 3-aminopropyltriethoxysilane, 8-hydroxyquinoline [63], 5-aminooindazole [90], benzotriazole [114], mercaptobenzothiazole [96,115,116], 2-mercaptobenzothiazole [117], thiophene derivatives [118], aspartic acid [119], 8-hydroxyquinoline [120], triazoles [121], α-aminocids [122] and 2-benzothiazylthio-succinate [123] have been incorporated as the anionic species in LDHs. These inhibitors can be incorporated in a single step during the synthesis of LDHs, or by a two-step process, where the LDH is formed and then through anion exchange the anionic inhibitors are introduced [31,98]. However, with the narrow spaces that exist between the interlayer galleries, it can be difficult to insert the larger organic inhibitors as anions. Ma et al. [90] used an interesting approach to incorporate the organic inhibitor 5-aminooindazole into the interlayer spacings of Mg-Al-LDHs. The authors initially formed the nitrate-intercalated Mg-Al-LDH. Next, the LDH was exfoliated to give single-layered nanosheets, enabling the stripping of the nitrates. Finally, the nanosheets were reassembled with the organic inhibitor. In addition, the anion exchange process depends on the nature of the anions. It is very difficult to exchange carbonate anions, and to a lesser extent, nitrate anions. The exchange of these anions normally involves a two-step process, with deintercalation of the carbonate or nitrate, followed by intercalation of the desired anion. For example, LDHs intercalated with CO$_3^{2-}$ can be transformed through calcination at about 500 to 550 °C to an oxide phase, as seen in Equation (8). The resulting oxide phase can then be rehydrated to restore, or partially restore, the original layered structure, while incorporating the desired anions [124]. However, this methodology is time-consuming and the LDH is not always fully restored.

$$\text{Mg}_{1-x}\text{Al}_x(\text{OH})_2(\text{CO}_3)_x/2 \rightarrow \text{Mg}_{1-x}\text{Al}_x\text{O}_{1+x/2} + x/2\text{CO}_2 + \text{H}_2\text{O}$$

(8)
As the anionic corrosion inhibitors are released from the LDH network, they are replaced by incoming anions, which are normally chloride anions [125]. This in turn gives rise to the entrapment of the aggressive chloride anions, as illustrated in Figure 6. This is a somewhat surprising but interesting concept. There is clear evidence that the release of the inhibitors provides good corrosion-protective properties, while the aggressive and unwanted chloride anions are trapped, and this can be beneficial in terms of mopping up aggressive chloride anions. However, if these chloride anions are subsequently exchanged with other anions, it may give rise to elevated chloride concentrations.

![Figure 6](image)

Figure 6. Schematic representation of the anion exchange process and trapping of corrosion-aggressive anion chlorides. Adapted with permission from Zou et al. [77], copyright Elsevier, 2019.

In addition, LDHs can be combined with oxidized Al substrates, where the Al substrate is first oxidized through a plasma electrolytic oxidation (PEO) process [126,127]. This is a rapidly growing research area, as LDHs can seal the pores in the PEO [127,128], and this leads to an improvement in corrosion protection. Furthermore, corrosion inhibitors can be introduced as the anions in the LDHs, exploiting their inhibitor release and self-healing properties. For example, Ferreira et al. [96] employed Zn-Al-LDHs loaded with vanadate anions to seal the pores in the PEO with intercalation of the vanadate anions into the pores. This sealing suppressed the corrosion process. In a related study, the same group devised a method to facilitate the growth of LDHs on thick PEO coatings on aluminum-based substrates [128]. This was achieved by using sol-gel chemistry to create an aluminum oxide-based xerogel on the PEO, which provided a source of aluminum ions to facilitate the nucleation of the LDHs. Likewise, PEO coatings have been formed on Mg alloys, or the alloys have been anodized to create the oxide phases and combined with LDHs to produce an improvement in the corrosion protection properties of Mg alloys [129–133]. Furthermore, LDHs have been employed to provide corrosion inhibition on PEO-coated Mg-LDH [134,135].

Although LDHs have been shown to be effective in corrosion protection, and the PEO-oxidized substrates enhance corrosion protection, the LDH network is porous, with intercalated water molecules. This in turn provides a pathway for the diffusion of oxygen, which can be reduced at cathodic sites. As this reduction reaction proceeds, the dissolution of the metal is promoted, leading to local acidification. As a result, degradation of the LDH film can occur. Various attempts have been made to suppress the diffusion pathway by adding additional components. One of the more successful additives is graphene, which has a sealing effect due to its impermeable nature [136–138]. In addition, the negative charge on graphene oxide (GO), combined with the positively charged LDHs, facilitates the in situ growth of LDHs on the GO sheets, creating a network that greatly reduces permeability and consequently enhances corrosion resistance [84]. In addition, nanoparticles such as WO$_3$ [139], zirconia [140] and Al$_2$O$_3$ [141] can also serve to inhibit diffusion within the LDH network.

In Table 2, some of the more recent LDH composites and their corrosion-protective properties are summarized. While pristine LDHs can provide corrosion-protective properties, their performance can be enhanced considerably by the addition of corrosion inhibitors and additives that can alter the diffusion pathway. As illustrated in Table 1, some of the lowest corrosion currents and/or highest resistance values are seen with added corrosion inhibitors [142], graphene [143] and metal organic frameworks (MOFs) [144].
Table 2. Summary of some recent LDH composites and their corrosion protection properties.

| LDH    | Additive          | Method                | Measure of Corrosion Protection                              | Ref.   |
|--------|-------------------|-----------------------|--------------------------------------------------------------|--------|
| Mg-Fe  | -                 | hydrothermal          | $R = 2.0 \times 10^3 \, \Omega \, \text{cm}^2$ Q325 steel   | [94]   |
| Ca-Al  | Mn                | co-precipitation      | $R = 5.2 \times 10^3 \, \Omega \, \text{cm}^2$ 2024-T3      | [104]  |
| Mg-Al  | Ni layer          | hydrothermal          | $R = 6.48 \times 10^3 \, \Omega \, \text{cm}^2$ AZ31B Mg   | [145]  |
| Mg-Al  | benzoate/perfluoro-decyltrimethoxysilane | hydrothermal | $|Z|/0.01Hz = 1.76 \times 10^6 \, \Omega \, \text{cm}^2$ AZ31 Mg | [69]   |
| Mg-Al  | 5-aminoindazole   | co-precipitation/hydrothermal | $R = 31 \times 10^5 \, \Omega \, \text{cm}^2$ $j_{corr} = 3.2 \times 10^{-7} \, \text{A cm}^{-2}/\text{Cu}$ | [90]   |
| Mg-Al  | Ce/NO$_3^-$       | co-precipitation      | $j_{corr} = 2.2 \times 10^{-7} \, \text{A cm}^{-2}$ AZ31 Mg alloy | [146]  |
| Mg-Al  | sodium dodecyl sulfate | co-precipitation/hydrothermal | $j_{corr} = 2.2 \times 10^{-8} \, \text{A cm}^{-2}$ $R = 4.38 \times 10^7 \, \Omega \, \text{cm}^2$ AZ31 Mg alloy | [142]  |
| Mg-Al  | 8-hydroxyquinoline/GO | hydrothermal          | $j_{corr} = 1.44 \times 10^{-9} \, \text{A cm}^{-2}$ AZ31 Mg alloy | [143]  |
| Mg-Al  | poly(ethyleneimine)/MXene, V$_2$O$_7^{2-}$ | hydrothermal          | $j_{corr} = 1.3 \times 10^{-8} \, \text{A cm}^{-2}$ $R = 3.2 \times 10^6 \, \Omega \, \text{cm}^2$ AZ31 Mg alloy | [147]  |
| Mg-Al  | albumin-WO$_3$    | co-precipitation      | $R = 4.46 \times 10^9 \, \Omega \, \text{cm}^2$ AZ31 Mg     | [139]  |
| Mg-Al  | 8-hydroxyquinoline/sol-gel | co-precipitation/hydrothermal | $R = 9.1 \times 10^6 \, \Omega \, \text{cm}^2$ AM60B alloy | [68]   |
| Zn-Al  | benzotriazole/(MOF)/polyvinyl butyral | co-precipitation/hydrothermal | $j_{corr} = 2.0 \times 10^{-12} \, \text{A cm}^{-2}/\text{Cu}$ | [144]  |

3.2. Transition Metal Dichalcogenides

In recent times, there has been considerable interest in TMDs, such as MoS$_2$, WS$_2$, MoSe$_2$, and WSe$_2$, because they possess properties similar to graphene in terms of their 2D sheet-like structures. MoS$_2$ has been employed in the protection of semiconductors, such as GaInP$_2$ (gallium indium phosphide), which are susceptible to chemical and electrochemical corrosion in aqueous electrolytes [148] and silicon-based photocathodes [149]. However, research into its applications in the corrosion protection of metals and alloys is still in its infancy. It has been shown in several studies that MoS$_2$ has excellent mechanical properties [150], making it an interesting candidate in the formulation of corrosion-protective coatings. Indeed, there is evidence from the literature to show that the addition of MoS$_2$ can improve the protective properties of coatings on metals or alloys [151–153].

In a recent study, Ding et al. [151] prepared MoS$_2$ nanosheets by exfoliating bulk MoS$_2$, followed by the collection of the 2D nanosheets through centrifugation. Then the nanosheets were combined with an epoxy curing agent to give a TMD/EP nanocomposite, which was painted onto steel and cured at 50 °C. The wt% of MoS$_2$ in the epoxy coating was varied, and it was found that the best corrosion protection was achieved with a 1.0 wt% MoS$_2$/EP. Using oxygen transmission and water vapor transmission rates, the impermeability of the prepared nanocomposite coatings was evaluated. The authors found that the MoS$_2$/EP coatings possessed good barrier properties, impeding the transport of both oxygen and water. The authors explained the observed corrosion protection in terms of reduced permeability and the low conductivities of the semiconductor TMDs, thus inhibiting galvanic corrosion, which is seen when graphene is employed in coatings [22]. In addition, it was concluded that the few layered MoS$_2$ nanosheets were ineffective in
catalyzing the oxygen reduction reaction. Similarly, Zhao et al. [154] found that epoxy coatings containing MoS$_2$ dispersed with sodium dodecyl benzene sulfonate reduced the water-permeability of the coating. Interestingly, greater adhesion between the coating and substrate was seen in the presence of the MoS$_2$, giving rise to a reduction in the rate of coating delamination.

Hong et al. [153] dispersed MoS$_2$ in sunflower oil, and applied this dispersion onto a stainless steel (SS 316L) substrate, which was then subjected to heating to polymerize the triglycerides in sunflower oil. As a result, an adherent polymeric coating with MoS$_2$-dispersed sheets/particles was formed. Good corrosion protection and durability was seen with the MoS$_2$-containing sunflower coating, and this was attributed to the formation of a highly ordered barrier coating. Likewise, ArunKumar et al. [155] dispersed MoS$_2$ and doped MoS$_2$ in sunflower oil, and found that doping MoS$_2$ with Fe, Co, and Ni ions resulted in an increase in the corrosion-protective properties of MoS$_2$. For example, the corrosion current of mild steel was measured as $83 \times 10^{-6}$ A cm$^{-2}$ in a chloride-containing solution. On modifying the steel with MoS$_2$, the current was reduced to $5 \times 10^{-9}$ A cm$^{-2}$, but it was reduced further to $3 \times 10^{-9}$ A cm$^{-2}$, $2 \times 10^{-9}$ A cm$^{-2}$ and $1 \times 10^{-9}$ A cm$^{-2}$ for Co-, Ni- and Fe-doped MoS$_2$, respectively. This is interesting, as metal ion doping generally increases the electrocatalytic activity of MoS$_2$ [156]. While this approach may be promising at short times, these more conductive metal-doped MoS$_2$ sheets may behave like graphene at longer times and promote galvanic corrosion.

On comparing WS$_2$ with MoS$_2$ in the formulation of corrosion-protective coatings on a Mg–Li alloy, Li et al. [157] found that a more compact and hydrophobic coating was formed with WS$_2$, to give significantly enhanced corrosion protection over an extended immersion time. Likewise, Prado and Virtanen [152] exploited the hydrophobic characteristics of MoS$_2$ to form a superhydrophobic metal matrix composite coating by adding MoS$_2$ particles to a copper matrix. This was then applied to two steel substrates, SS 316L and CS N80. It has also been shown that the addition of MoS$_2$ has beneficial effects in the performance of polyvinyl butyral and zinc-rich polyvinyl butyral coatings [158]. Furthermore, on incorporating MoS$_2$ into conducting polymers, such as polypyrrole and polyaniline, their protective properties can be enhanced [159,160]. In these cases, MoS$_2$ was incorporated during the electropolymerization step, and it has been suggested that the MoS$_2$ blocks voids within the porous polymers, reducing the transport of oxygen and water to the substrate [159].

Given the semiconducting properties of TMDs, they are attractive in photoelectrochemical cathodic corrosion protection [74]. This is similar to cathodic protection, where a potential or current is applied to the metal surface to polarize it below its corrosion potential and into the immune region (Figure 7) [161]. In photocathodic protection, electrons are excited from the valence band into the conduction band of the n-type semiconductor, and these are then coupled with the corrosion-susceptible metal or alloy, resulting in polarization into the immune region. Compared to sacrificial anodes, which provide corrosion protection by preferentially dissolving and producing metal ions while protecting the desired metal, photocathodic protection is environmentally acceptable.

TMDs such as MoS$_2$ have small band gap energies, and therefore the electron and hole pair can be generated using visible light. For example, MoS$_2$ has been combined with TiO$_2$ to facilitate the absorption of visible light, and to suppress the recombination of electron-hole pairs in TiO$_2$. This is achieved by forming a p-n heterojunction with TiO$_2$ to give separation of the photogenerated carriers [74]. It has been shown that on absorption of visible light, the potential of the SS304 substrate coupled to the MoS$_2$/TiO$_2$ nanocomposite dropped by approximately 500 mV, giving cathodic protection. Furthermore, when the light source was removed and then turned on again, the same potential drop was observed, indicating very good stability of the MoS$_2$/TiO$_2$ nanocomposite.
3.3. MXenes

MXene nanosheets have a rich surface chemistry, large specific surface areas, and very good mechanical properties with good thermal and electrical conductivity. They are attracting a lot of attention in corrosion research, especially as additives in polymer composites. MXenes have a unique multilayer structure, which is composed of numerous parallel sheets, as illustrated in Figure 2C. These sheets can act as a barrier to the diffusion of oxygen and aggressive ions, such as chlorides. Indeed, Yan et al. [72] observed a considerable reduction in the corrosion current from $7.51 \times 10^{-5}$ A cm$^{-2}$ for bare Q345 to $3.38 \times 10^{-8}$ A cm$^{-2}$ for 1.0 wt% Ti$_3$C$_2$/epoxy. The 1.0 wt% MXene coating also exhibited the highest charge transfer resistance, with a value of $5.48 \times 10^8$ Ω cm$^2$ after 2 h and $2.82 \times 10^7$ Ω cm$^2$ after 96 h.

It is also possible to encapsulate molecules and ions between the MXene layers, and this can be exploited to load corrosion inhibitors that can be subsequently released in response to a corrosion event. For example, Haddadi et al. [64] functionalized Ti$_3$C$_2$ with NHz groups and loaded the MXene with Ce$^{3+}$, a well-known corrosion inhibitor. The Ce$^{3+}$-containing MXene was dispersed in epoxy to provide a coating. The protective properties of the epoxy coating, EP, MXene-EP and MXene-EP-Ce$^{3+}$ were compared. The corrosion current was reduced from $15.65 \times 10^{-6}$ A cm$^{-2}$ to $13.90 \times 10^{-6}$ A cm$^{-2}$ upon incorporation of the MXene, and reduced further to $3.16 \times 10^{-6}$ A cm$^{-2}$ with the addition of Ce$^{3+}$. Using a combination of Ce$^{3+}$ release studies and impedance and salt spray tests, the authors clearly showed that MXene-EP-Ce$^{3+}$ was the superior coating. This was attributed to the release of the Ce$^{3+}$, which acts as a cathodic inhibitor. This is illustrated in Figure 8.

Furthermore, MXenes can be functionalized using their terminal groups [162,163]. Recently, epoxy-functionalized Ti$_3$C$_2$ nanosheets were formed by grafting the MXene with (3-glycidyloxypropyl) trimethoxysilane [72]. This functionalized MXene was then incorporated into an epoxy coating. It was found that the functionalized MXene gave the highest corrosion protection, when compared to the non-functionalized MXene. This was explained in terms of higher dispersibility and chemical bonding within the matrix with the functionalized MXene. Other functionalized groups have been successfully employed, and these include L-cysteine [164], chitosan [165], and amino groups [166]. These are normally covalently attached to the surface of MXenes, and then incorporated within an epoxy to make well-dispersed nanosheets with good barrier protection properties. In addition to epoxy coatings, MXenes have also been combined with silane-based coatings to improve the quality of silane-based systems. The hydrophilic groups on the MXene give rise to good dispersion of the MXene in the silane coatings, and this avoids structural defects.
MXenes have been introduced into silane films using γ-glycidoxypropyltrimethoxysilane to deposit composite coatings on AA2024 aluminum alloy [167], and applied to copper using 3-mercaptopropyltriethoxysilane (mercaptosilane) [168]. The Ti₃C₂Tx/silane composite films have been shown to exhibit excellent adhesion and corrosion resistance, and can be prepared using a simple solution-based process.

![Schematic representation of the corrosion-inhibition mechanism of Ti₃C₂Tx MXene loaded with Ce³⁺ in the coating, with the released Ce⁵⁺ acting as a cathodic inhibitor. Adapted with permission from Haddadi et al. [64], copyright American Chemical Society, 2021.](image)

Figure 8. Schematic representation of the corrosion-inhibition mechanism of Ti₃C₂Tx MXene loaded with Ce³⁺ in the coating, with the released Ce⁵⁺ acting as a cathodic inhibitor. Adapted with permission from Haddadi et al. [64], copyright American Chemical Society, 2021.

Nevertheless, Ti₃C₂Tx has high electrical conductivity, a hydrophilic surface, is prone to oxidation, has a natural restacking tendency and has relatively poor stability in water. These are characteristics that are not always desirable in the formulation of protective coatings. In particular, the high conductivity can promote corrosion, with the formation of a galvanic corrosion cell with the substrate. Indeed, there have been reports which clearly show that MXenes can facilitate corrosion [64]. By studying the interface interactions between Ti₃C₂Tx and Fe, Cai et al. [64] showed that the corrosion of Q345, a mild steel, was accelerated by Ti₃C₂Tx. This was explained in terms of the high conductivity of MXene, which facilitated the oxygen reduction reaction, an important half-cell reaction in the corrosion cell.

Recently, there has been much focus on enhancing the stability of MXenes. Ti₃C₂Tx MXene nanosheets are prone to oxidation in both air and water, and this oxidation reaction can give rise to the formation of oxides that can lead to further degradation of the MXene layered structure. This reduces the barrier protection afforded by the MXene sheets when used in protective coatings. Attempts have been made to enhance the corrosion protection properties of MXenes, and one methodology involves the formation of MXene hybrids or heterostructures. MXenes have been combined with several other materials, including carbon dots (CD) [169], graphene oxide (GO) [170], LDHs [172], h-BN [173], MoS₂ [174] and conducting polymers [175] to form composites or heterostructures. The addition of this second material can enhance the corrosion-protective performance of MXenes. For example, it is well known that MXenes are susceptible to hydrolysis reactions and have poor stability in water. The chemical stability of MXenes in water has been improved by using carbon dots (CD) to functionalize Ti₃C₂Tx MXene and form a CD-Ti₃C₂Tx hybrid [169]. Likewise, an OH-group-modified h-BN was utilized to reduce the formation of a conducting MXene network [173]. With the addition of LDHs, Ti₃C₂Tx MXene/Mg-Al-LDH heterostructures can be formed [172], as shown in Figure 9. These
inhibit the restacking of the MXene to give very good dispersion throughout the coatings, with good compatibility with epoxy resin materials. Moreover, anionic corrosion inhibitors can be loaded onto LDHs. Restacking of MXenes can also be minimized by forming hierarchical Ti$_3$C$_2$T$_x$/MoS$_2$ heterostructures [174]. The interconnected MoS$_2$ nanosheets were anchored onto the MXene nanosheets, and as a result effectively prevented restacking of both the MXene and the MoS$_2$ nanosheets. On using this heterostructure as a filler in an epoxy coating, good anti-corrosion and anti-wear properties were observed. Using intercalation polymerization, aniline was polymerized to give polyaniline layers between the Ti$_3$C$_2$ sheets [175]. This was shown to reduce the conductivity of the MXenes, which is necessary to achieve long-term corrosion protection. It has been shown that ionic liquids, such as imidazolium salts, can passivate the MXenes, while the imidazolium salts can also act as corrosion inhibitors. Zhao et al. [176] have used this approach to form air-stable MXene-reinforced coatings. Not only did the ionic liquid protect the MXene from oxidation, it also provided good dispersion, increasing the barrier property of the coating with an additional self-healing capacity, due to the inhibiting properties of the imidazolium-based ionic liquid.

![Figure 9. Schematic representation of the synthesis of (a) the Ti$_3$C$_2$T$_x$ MXene nanosheets and (b) formation of the Ti$_3$C$_2$T$_x$/Mg-Al-LDH heterostructure. Reprinted with permission from Cai et al. [172], copyright American Chemical Society, 2021.](image)

### 3.4. Hexagonal Boron Nitride

Nanosheets of hexagonal boron nitride (h-BN) have similar characteristics as graphene, in terms of mechanical, thermal, hydrophobic and permeability properties. However, h-BN is an insulator, and this is one significant difference that makes h-BN more attractive than graphene as a component of coatings or protective films. With its insulating properties, it is very unlikely to promote galvanic corrosion. However, the lack of functional groups on the h-BN sheets make it difficult to functionalize the surface, compared to the ease at which GO can be functionalized. Furthermore, it can be difficult to disperse h-BN in aqueous solutions or waterborne epoxy matrices, owing to its hydrophobicity and strong interlayer van der Waals interactions.

Different approaches have been employed with the aim of forming stable dispersions of h-BN that can be employed in protective coatings. For example, it is possible to employ a non-covalent method whereby a suitable organic molecule is used to modify the h-BN nanoplatelets through π-π interactions. This has been achieved with amine-capped aniline trimers, resulting in a stable dispersion of h-BN nanoplatelets in organic solvents. This dispersion was subsequently used to form a 1.0 wt% h-BN/epoxy coating with good barrier properties, and good wear and corrosion resistance [177]. Similarly, a homogeneous dispersion of h-BN in an epoxy matrix was obtained using a water-soluble carboxylated aniline...
Again, this good dispersion was attributed to strong π-π interactions between h-BN and the trimer. Poly(2-butyl aniline) (PBA) [58] and furfuryl methacrylate [179] have also been employed to give well-dispersed h-BN in epoxy coatings, while ionic liquids, with their conjugated structures and nitrogen atoms, facilitate π-π interactions with the h-BN nanoplatelets [180]. In addition, GO, with hydrophilic characteristics, was employed as an intercalator to exfoliated h-BN and enhanced its dispersion. The π-π interactions between GO and h-BN gave rise to h-BN/GO stacks [181].

Alternatively, the h-BN can be chemically functionalized. Using this approach, Zhao et al. [182] employed a gas-assisted liquid exfoliation method to create hydroxyl-functionalized h-BN, which was subsequently phosphorylated. Wu et al. [183] and Yu et al. [184] treated h-BN with (3-aminopropyl) triethoxysilane (APTES) to functionalize its surface with an alkoxyisilane, in order to create a homogenous dispersion of the functionalized h-BN in epoxy coatings. In addition, a Lewis acid–base reaction was performed to functionalize h-BN with water-soluble branched poly (ethyleneimine) [185], while h-BN was functionalized with polyacrylic acid through a plasma polymerization reaction [186]. It has also been shown that h-BN can be modified with epoxy groups and polydopamine, which is readily formed through the self-oxidation of dopamine in an alkaline solution. This relatively simple method was reported to provide good compatibility between the h-BN and the epoxy matrix, resulting in impressive corrosion-protective performance. These non-covalent and covalent modifications of h-BN enhance its dispersion in epoxy [58,178,180,181,183,185,187] and acrylic [186] coatings, giving rise to good corrosion-protective properties. The enhanced anticorrosive performance has normally been attributed to the homogeneously dispersed h-BN nanoplatelets, which provide very good water- and oxygen-barrier properties.

Other polymeric formulations have been employed with h-BN, and these include polyvinyl alcohol [76], polyimide [188], polyvinyl butyral [189] and waterborne polyurethane [190]. Using spin coating, Husain et al. [76] coated SS 316L with h-BN dispersed in polyvinyl alcohol (PVA). The PVA was used as a binder to increase the adhesion between the h-BN nanoplatelets and the steel surface. It was concluded that the h-BN films were effective at inhibiting corrosion. However, crevice and pitting corrosion were observed between the metal and coating interface. Interestingly, when h-BN was dispersed in waterborne polyurethane [190], the coating was shown to provide long-term corrosion protection for the underlying copper.

Protective h-BN deposits have also been deposited directly onto the substrate by using electrophoretic deposition [182]. In this case, dispersed h-BN and dispersed phosphorylated h-BN were electrophoretically deposited onto Q235 carbon steel substrates at applied potentials between 0.6 and 1.2 V. The corrosion current for the unmodified substrate was 17.74 × 10^{-6} A cm^{-2}, but lower values of 2.88 × 10^{-6} and 0.55 × 10^{-6} A cm^{-2} were observed for the electrophoretically-deposited h-BN and phosphorylated h-BN, respectively. However, with increasing immersion time, delamination of the deposits was observed. Magnetron sputtering has also been employed to deposit h-BN directly onto stainless steel (SS304) substrates [191]. These deposits showed good corrosion resistance over a 10-week period when immersed in a 3.5 wt% NaCl solution. Huang et al. [192] formed atomically thin h-BN films at 1000 °C and 1100 °C on solid and melted copper. The authors found that the quality of the h-BN atomic thin films was important, with water dissociation reactions evident at h-BN boundaries, leading to oxidation of the copper substrate. On the other hand, less-defective, high-quality films grown on melted copper showed impressive corrosion protection in 0.5 M NaCl.

Iron oxide nanoparticles (Fe₃O₄) have been combined and supported on h-BN to create corrosion-protective coatings [193]. Zhang et al. [193] employed hydrothermal synthesis to form Fe₃O₄ nanoparticles on the surface of h-BN. The h-BN-Fe₃O₄ hybrids were incorporated as fillers into epoxy resin to create protective coatings. The good corrosion protection was explained in terms of blocking of the micro-pores within the coating. The Fe₃O₄ nanoparticles supported on the h-BN nanoplatelets were less prone to
agglomeration, providing a more homogenous dispersed phase that reduced the transport of oxygen, water and aggressive chloride ions through the epoxy coating.

As h-BN and graphene share similar properties, direct comparisons of their anti-corrosion performance have been made [184,194–196]. Yu et al. [184] functionalized graphene, graphene oxide and h-BN with 3-aminopropyltriethoxysilane to form a series of waterborne epoxy composite coatings on Q235. Using a combination of Tafel analyses, electrochemical impedance spectroscopy measurements and immersion polarization plots depicted in Figure 10. Similarly, Sheng et al. [204] formed polydopamine-modified g-C\textsubscript{3}N\textsubscript{4} on an aluminum substrate for a 20 day-period. It is normally the exfoliated 2D structures that are employed in the design of coatings, as they have the potential for more chemical interactions with other materials, enabling synergistic effects, and a much higher surface area compared to the bulk g-C\textsubscript{3}N\textsubscript{4}. Nevertheless, agglomeration of the g-C\textsubscript{3}N\textsubscript{4} nanosheets can easily occur, and this is a particular issue with water-based epoxy coatings [201]. As agglomeration occurs, the corrosion-protective efficiency of the nanocomposite coatings decreases significantly. The bulk g-C\textsubscript{3}N\textsubscript{4} can be exfoliated in alcohols, such as isopropanol [202], but it is more challenging to maintain the 2D nanosheets dispersed in coating formulations or the final coatings. One approach that has been employed involves the use of a companion material [198,203]. For example, graphene oxide, which is hydrophilic as a result of its acidic functional groups, can facilitate the dispersion of g-C\textsubscript{3}N\textsubscript{4} in waterborne epoxy polymers [198]. It was shown by XRD measurements that a GO/g-C\textsubscript{3}N\textsubscript{4} nanohybrid was formed, with the g-C\textsubscript{3}N\textsubscript{4} nanosheets remained evenly dispersed for over 24 h. Very good corrosion protection was observed with the added polydopamine, and this was ex-
plained in terms of strong interfacial bonding between the polydopamine and epoxy matrix, combined with very good barrier protection from the nanofillers. Other materials used to enhance the dispersion of g-C$_3$N$_4$ in waterborne coatings or to enhance its mechanical properties as a filler include polyaniline formed on the surface of g-C$_3$N$_4$ [203], molybdenum oxides, MoO$_x$ [205], and SiO$_2$ with TiO$_2$ [206]. Also, g-C$_3$N$_4$ has been functionalized with ethylenediamine vapor to enhance its dispersion in a solvent-based epoxy [207]. Clearly, the 2D g-C$_3$N$_4$ nanosheets can be hybridized with other components to design more corrosion-protective coatings.

Figure 10. Schematic illustration of the preparation of the g-C$_3$N$_4$ nanocomposite (left) and polarization curves recorded after 15 days of immersion in an aqueous 3.5 wt% NaCl solution. Reprinted with permission from Xia et al. [201], copyright Elsevier, 2020.

As a photocatalyst, g-C$_3$N$_4$ is attracting considerable attention [208], and it has been studied and successfully employed in the photocathodic protection of SS316 and Q235 [209], Q235 CS [210] and SS 304 [75]. It has a relatively high charge carrier recombination rate, and therefore it is mostly combined with other semiconductors to create heterostructures. In a recent study, a g-C$_3$N$_4$/GO/MoS$_2$ composite was formed, and generated a photocurrent of 77.19 $\mu$A cm$^{-2}$ when coupled with SS 304. In this case, the photogenerated electrons in the conduction band of g-C$_3$N$_4$ were transferred to the valence band of MoS$_2$, giving effective charge separation [75]. Other heterojunctions, including ZnO/g-C$_3$N$_4$ [211] and In$_2$O$_3$/g-C$_3$N$_4$ [212], have been utilized in photocathodic protection. Interestingly, Zhang et al. [209] formed g-C$_3$N$_4$ $n$-$n$ homojunction films on indium tin oxide substrates. With the optimum photocathodic protection, photocurrents of 143.44 $\mu$A cm$^{-2}$ and 111.48 $\mu$A cm$^{-2}$ were observed for SS316 and Q235, and the potentials were lowered to $-982$ mV and $-1081$ mV, well into the immune region for SS316 and Q235.

4. Conclusions, Outlook and Future Directions

The corrosion of metals and alloys has always been an issue, but in recent years corrosion protection has emerged as a particular challenge, given the increasing focus on sustainability and environmental issues. Many of the corrosion-protective approaches used in the past have relied on chromates and volatile organics that are no longer environmentally acceptable. At the same time, metals and alloys have to function in new and extremely harsh environments, such as the blades of windmills, plates in fuel cells, or casings of batteries. While significant advancements have been made in structural materials, in terms of their mechanical properties, their ability to perform and withstand corrosion remains a particular challenge.

Fortunately, there has been an explosion in the development of new materials, spanning various nanostructured materials and 2D materials, and these are likely to contribute
to developments in corrosion protection in the near future. It is clear that the layered and 2D materials reviewed here are emerging as promising materials, and may provide new, environmentally-acceptable coatings that can protect metals and alloys. These 2D materials have been successfully employed in the formulation of anticorrosion coatings, frequently acting as coating fillers and impermeable sheets that increase barrier protection and reduce diffusion of oxygen, water and aggressive ions throughout the coating. They have been studied in different aggressive environments and at elevated temperatures, and have performed well. While 2D graphene has been studied extensively, there is now a consensus that the conducting properties of graphene promote galvanic corrosion with the substrate, and can in fact increase the corrosion rate. Therefore, 2D materials that have much lower conductivity than graphene, including h-BN, g-C₃N₄, and LDHs, are interesting, as they are unable to generate galvanic cells with the substrate, and may play a leading role in the development of new anticorrosion coatings. Relatively few studies have centered on evaluating TMDs in corrosion protection, and clear evidence to suggest that TMDs can provide corrosion protection is still lacking. Nevertheless, they have been employed to create superhydrophobic coatings, which is very relevant in the development of anticorrosion coatings. In terms of photocathodic corrosion protection, TMDs and g-C₃N₄, which exhibit semiconducting characteristics, are interesting. The band gap energies of both TMDs and g-C₃N₄ are small, and the necessary charge carriers can be generated using visible light.

Nevertheless, the true applications of these materials in corrosion protection are only emerging, and require further study before they can be applied extensively in the formulation of anticorrosion coatings. One avenue that requires further study, and is relevant to all 2D materials, is the exfoliation of the 2D sheets to give stable, well-dispersed sheets in organic and especially in waterborne coatings, which are more environmentally acceptable. When homogeneously dispersed, the 2D sheets can impede diffusion, however if the sheets become agglomerated their effectiveness is reduced considerably. Furthermore, the exfoliation efficiency of 2D materials can be low and require organic solvents, which limits the dispersion of 2D materials in waterborne coatings. On the other hand, LDHs are employed as layered materials. With this layered structure, corrosion inhibitors can be incorporated into the layered structure and released at corroding sites. However, this approach can lead to the incorporation and trapping of chloride anions. While this has the potential to mop up chloride anions, the longer-term impact of these trapped aggressive anions requires further study.

Another challenge is the synthetic processes required to generate both the parent and the 2D materials. The development of synthetic processes that can be easily upscaled and are cost-effective are essential. Therefore, high temperatures or high pressures that are typically employed with h-BN and the parent MAX phase of MXenes make these materials less cost-effective. The lower temperature methodologies, such as co-precipitation, although simple to carry out, have complex chemistry, making it more challenging to upscale the processes.

While challenges remain, it is clear that these 2D materials are likely to play a significant role in the development of protective and anticorrosion coatings into the future, as new synthetic methods for the functionalization of 2D materials are developed, facilitating their improved dispersion in coating formulations.

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