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Low-temperature synthesis of a graphene-based, corrosion-inhibiting coating on an industrial grade alloy

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The use of graphene materials as protective coatings for metallic substrates has received much attention because of graphene's ability to seal a metal and prevent the diffusion of most corrosive species to the metal surface. The application of graphene-based coating technology to industrially relevant samples, however, is hindered by the high growth temperatures required to prepare functional and efficient protective graphene layers. The growth temperatures typical for popular catalysts and precursors are incompatible with most relevant alloys. Here, we present a low-temperature synthesis route to a graphene-based coating, using a complex metallic alloy, Inconel 625, as an example substrate. We demonstrate that the coating reduces the sample corrosion current by two orders of magnitude and also shifts the open circuit potential from -308 mV to +129 mV. We present an extensive characterisation of the coating and the coating synthesis procedure. The procedure relies on a surface-activated, thermally-induced polymerisation reaction and the method should be transferable to other metallic alloys.

Introduction

Graphene is a two-dimensional (2D) material, consisting of carbon atoms arranged in a honeycomb structure.¹ Graphene has been shown to function as a protective coating for several metal substrates, including alloys, towards a range of gases, water and saltwater.^{2–5} A defect-free graphene sheet may entirely isolate the metal from its environment as it is impermeable to all gas molecules, including helium, as well as a large number of reactive and corrosive species.^{6,7}

Direct growth of graphene materials on test substrates has been shown to be more successful at preventing corrosion than

graphene coatings transferred from a growth substrate to the test substrate.⁵ The direct growth of large-scale high-quality graphene coatings often relies on chemical vapour deposition (CVD) methods. CVD methods describe the heating of a substrate in the presence of a gaseous carbon source, such that the thermally activated surface catalyses the chemical conversion of the carbon source into a graphene sheet. This process, however, often requires substrate temperatures of 700 °C and above to produce high quality graphene sheets.⁸ These high temperatures are detrimental to many of the alloys

commonly used in industrial processes. The high temperatures lead to changes in the micro-composition, and structure of an alloy and hence CVD may not be a suitable means to coat many industrially relevant, corrosion prone alloys.⁹ In addition, the growth of a defect-free graphene sheet on alloys via CVD methods is not straight forward. Defects provide access channels for corrosive species to reach the metallic substrate, which has been shown to increase corrosion rates.¹⁰ Once penetrated, the graphene sheet may then act to encapsulate the reactive species at the surface, while simultaneously accelerating galvanic corrosion of the metal. This is facilitated by the high nobility and electron mobility of graphene.¹¹ One proposed solution to this problem is to prepare thick multi-layered graphene sheets, increasing the time required for diffusing species to reach the metal interface.^{12,13} In short, high growth temperatures will ruin the alloys, while low temperatures will ruin the graphene.

This dilemma can be solved by developing a method for direct growth of multi-layered graphene, and graphene-like coatings on industrial samples using lower growth temperatures.^{14,15} Ni/Cr alloys of the brand Inconel 625 are highly resistant towards oxidation and corrosion in aqueous environments but are known to be susceptible to corrosion in acidic environments.^{16,17} This brand of alloys is expensive to produce and, moreover, is used in a wide range of hostile environments including nuclear, super-critical water and marine operations.^{18,19} The high corrosion resistance of Inconel 625 stems from the intrinsic, thick passivation layer formed by metal oxides during alloy production^{20,21} and a complex interaction between the metal species during preparation of the material.

Our scheme for low-temperature graphene growth relies on deposition of an sp^2 carbon source directly onto the substrate. The polycyclic aromatic hydrocarbon, coronene, is used as the carbon source. We show that the annealing of a thick film of coronene yields a continuous network of micrometer sized graphene-like carbon-based domains that constitute the anti-corrosion coating. Such a substrate-induced polymerisation reaction, using polycyclic aromatic hydrocarbons as a carbon source to produce graphene films, has been previously reported for growth on Cu substrates.²² Here we report on the corrosion resistance of this graphene-like coating on Inconel through exposure of the surface to HCl. A comparison with non-coated, control samples demonstrates that the coating is an efficient means to enhance the corrosion resistance of the alloy.

Experimental

Polycrystalline Inconel 625 sample pucks, 9 mm in diameter and 1 mm thick, were mechanically polished to a mirror finish using SiC abrasives. The Inconel 625 alloy has a nominal composition of Ni 58 wt%, Cr 20-23 wt%, Mo 8-10 wt%, Fe 5 wt%, Nb 3-4 wt%, Co 1 wt%, with trace amounts of Mn, Si, Al, Ti and C. After polishing, samples were sonicated in ethanol. No further treatment of the samples, hereafter labelled “pristine”, was performed and these samples are used throughout the study as control samples. A second batch of samples was cleaned in an ultra-high vacuum chamber, with a base pressure below 10^{-9} mbar. The chamber is equipped with an ion sputter gun, an Auger electron spectrometer (AES - Perkin-Elmer single-pass cylindrical mirror analyzer, model 10-155 used with an emission current of 2.1 mA and a beam voltage of 2500 kV), a manipulator, which allows for controlled sample heating and

cooling, and a Knudsen cell molecular evaporator for deposition of coronene onto the sample surface. Several cycles of sputtering (with Ne^+ at a kinetic energy of 1.5 keV) followed by annealing to 550 °C were used to remove the intrinsic oxide layer on pristine samples and to produce samples labelled throughout as “clean”.

Coronene (Sigma-Aldrich; powder with 99% purity) was used as the carbon source for all experiments. A small sample of powder was placed behind a bead of quartz wool in a Knudsen cell molecular evaporator equipped with a nozzle for targeted dosing. The coronene powder was thoroughly degassed at 100 °C to remove residual solvents. During molecular deposition on Inconel sample pucks, the molecular doser was heated to 170 °C and the sample placed directly in front of the targeting nozzle. Deposition continued until a visible, multilayer molecular film appeared on the sample surface. The film appeared as pale yellow-green under ambient light but was clearly visible as a fluorescing blue-green spot under UV light. The sample was kept at room temperature during deposition and then annealed, at 1 °C/s, to progressively higher temperatures, cooling to 60 °C after each temperature was reached. The progressive steps involved heating to 122 °C, 150 °C, 175 °C, 225 °C and finally 350 °C to produce the coating. Samples prepared like this are labelled throughout as “coated”.

Optical microscopy was performed using a Nikon Eclipse Ci microscope and a 10x magnification objective. Scanning electron microscopy (SEM) images were collected using an FEI Nova NANO SEM 600 with a through-the-lens detector and a beam energy of 5.00 kV at various magnifications. Raman spectroscopy was obtained using a Renishaw Invia Reflex Raman Spectroscopy System. All spectra were obtained using a 457 nm Ar-ion laser with a 2 s acquisition time and 150

accumulations per spectrum through a 100x objective. The spectra shown have been analysed with Renishaw Wire 4.1 software. They have been corrected for any cosmic rays, peaks arising from vibrational modes attributed to atmospheric oxygen and nitrogen have been removed, and a background was described using a 4-order polynomial and was subsequently subtracted. The spectra were then lightly smoothed using adjacent averaging.

X-ray photoelectron spectroscopy (XPS) was performed at the MATLine beamline, ASTRID2 Aarhus, Denmark. Photoelectron intensity was measured from the C1s, O1s, Ni3p and Cr3p core levels using photon energies of 375 eV, 610 eV, 150 eV and 150 eV respectively. Spectra were analysed using KolXPD, where linear (Shirley) backgrounds were subtracted for the C1s, O1s (Ni3p, Cr3p) spectra, and core level intensity was deconvoluted into constituent peaks.

Both polarization curves and electrochemical impedance spectroscopy (EIS) were carried out to test the corrosion performance of both pristine and coated Inconel samples using a Gamry Reference 3000 potentiostat and an ECM8 Electrochemical Multiplexer. A typical three-electrode set up was applied, using a Ag/AgCl reference electrode, a platinum counter electrode, and Inconel samples as working electrode. A 5 wt% hydrochloric acid solution was used as the electrolyte. Polarization curves were measured after the open circuit potential (OCP) was stabilized and the potential was scanned from -300 mV to 300 mV (vs. OCP) with a scan rate of 1 mV/s. EIS measurements were performed under ± 10 mV sinusoidal perturbation applied at the recorded OCP of the sample. The frequency was scanned between 100,000 Hz and 0.01 Hz with 10 points per decade. Both Tafel fitting of polarization curves and equivalent electrical circuit (EEC) fitting of EIS results were

carried out with Gamry Echem Analyst software.

Results and discussion

Pristine Inconel

Optical microscopy and SEM images of pristine samples are shown in **Fig. 1**. Both images show only straight lines of varying orientations, identified as scratch marks from the mechanical polishing. There are no indications of grain structure or carbide inclusions on the surface²³

XPS data for pristine samples are shown in **Fig. 2**. The data show the presence of C and O contaminants at the sample surface with full peak descriptions given in **Table 1**. The C1s spectrum was fit predominantly with a single peak, consisting of a Doniach-Šunjić function convoluted with a Gaussian function. The peak has a binding energy of 284.77 eV, a Gaussian full width half maximum (FWHM) of 1.13 eV and a Lorentzian FWHM of 0.48 eV. Intensity also peaks at 288.22 eV and is assumed to arise from oxidised carbon contaminants on the sample surface.^{16,24} The O1s spectrum can be fit with two Gaussian functions. Both peaks represent the formation of Cr oxides, as expected for a pristine Inconel 625 sample.^{25,26} A full metal analysis of the pristine sample was hampered by the presence of the thick passivating chromium oxide layer intrinsic to the material. The XPS signal arising from this Cr layer is also shown in **Fig 2** and only Cr oxide peaks are observed.^{16,24}

Figure 1: a) Optical and b) SEM microscopy images from pristine Inconel 625 samples. Only scratch marks originating from mechanic polishing are visible.

Figure 2: Photoelectron intensity from the C1s, O1s and Cr3p core levels at the surface of a pristine Inconel 625 sample. The raw data, in red, is fit using deconvoluted peaks described in detail in table 1.

It was necessary to remove the oxide layer intrinsic to the Inconel surface prior to the thermal polymerisation step in order to ensure coating growth. Hence, we now present a characterisation of the clean surface. The derivative of the Auger electron

spectrum from a pristine sample and a clean sample are compared in **Fig. 3**. The pristine sample shows peaks representative of C KLL series around 285 eV, the O KLL line at 507 eV, as well as peaks from the Cr LMM and Ni LMM series.²⁷ After cleaning, the peak at 507 eV, representing O KLL, drops dramatically and new peaks from the Mo MNN series appear in the spectrum between 146 eV and 219 eV.²⁷ In addition, the shape of the peaks in the C KLL series changes, as illustrated in the inset to the figure. The broad peak at 268 eV in the spectrum from the pristine sample transforms into three distinct peaks in the clean sample. The broad peak at 268 eV is characteristic of graphitic carbon, while the C KLL peak shape for the clean sample is more characteristic of metal carbides.^{28,29} All of the metal peaks increase in intensity, narrow slightly and shift to higher energies upon cleaning. This, in combination with the reduction in the O peak, signifies the removal of the passivating oxide layer intrinsic to pristine Inconel 625, upon cleaning via sputter and anneal cycles under UHV conditions.

XPS data from a similarly cleaned sample are presented in **Fig. 4**. The C1s is relatively low in intensity and can now be fit, predominantly, with two Gaussian functions. The binding energies of both components (282.67 eV and 283.74 eV) are characteristic of metal carbides, which concurs with measurement from AES in relation to **Fig. 3**.^{30,31} The O1s spectrum can be deconvoluted into 4 separate Gaussian functions. The two higher binding energy peaks (530.39 eV and 531.84 eV) are attributed to Cr oxides, while the lower binding energy peaks are attributed to Ni oxides (529.34 eV and 528.00 eV).³²

The metal core levels, Ni3p and Cr3p, both show intensity characteristic of clean metals; Ni at 66.00 eV and Cr at 41.97 eV, with small shoulders at higher binding energies characteristic of the respective oxides.³³ This is in keeping with the AES data in **Fig. 3**, and confirms that it was not possible to completely remove all oxide species from the surface under these cleaning conditions.

To test the response of this surface to a controlled exposure to O₂, the clean sample was exposed to 1500 L of O₂ at a background gas pressure of 2E-6 mbar with the sample at room temperature. The core levels were checked afterwards with XPS and the results, in **Fig. 4b**, show that only the Cr3p core level shows any significant effect. While other core levels remain relatively unchanged, the Cr3p spectrum shows a reduction in the clean Cr peak and a rise in a new Cr oxide peak at 42.92 eV, after O₂ exposure. We note that it is not possible to compare the intensities of the photoelectron signal between figures.

Figure 3: AES data comparing pristine and clean Inconel 625 samples. The clean sample results after several cycles of sputtering and annealing, as described in the text.

Figure 4: XP spectra for the C1s, O1s, Ni3p and Cr3p core levels in a) a clean Inconel 625 sample and b) the same sample after exposure to 1500 L O₂ at room temperature. The peak assignments are described in the text and in the table 1.

Table 1. Deconvoluted peak binding energies and FWHM (Binding energy / eV (FWHM / eV)) used to describe all photoelectron signals from the core levels studied during XPS experiments.

CORE LEVEL	C1S	O1S	CR3P	NI3P
Pristine	284.75 (1.09) graphic C ³⁴ 288.20 (1.74) organic C ³⁵	531.93 (2.20) Cr oxide ³² 529.90 (1.55) Ni oxide ³²	53.63 (1.54) oxide ³⁵ 44.90 (2.14) oxide ³⁵	
Clean	282.67 (1.18) carbides ^{30,31} 283.74 (1.70) graphic C	529.34 (1.55) Ni oxide 530.39 (2.00) Cr oxide 531.84 (2.20) Cr oxide 528.00 (1.66) Ni oxide	41.97 (1.37) metallic ³³ 53.63 (1.54) oxide 44.90 (2.14) oxide	66.00 (1.60) metallic ³³ 67.72 (1.60) oxide ³⁵ 68.05 (1.50) oxide ³⁵
O₂ dose in UHV	282.66 (1.24) carbides 283.73 (1.70) graphic C 288.20 (1.74) organic C	529.38 (1.55) Ni oxide 530.39 (2.00) Cr oxide 531.57 (2.20) Cr oxide 528.00 ((1.66) Ni oxide	44.90 (2.14) oxide 41.97 (1.37) metallic 42.92 (1.37) oxide 43.63 (1.54) oxide	66.00 (1.70) metallic 68.05 (1.70) oxide 67.72(1.70) oxide

Coating after air exposure	284.77 (1.13) graphitic C	528.55 (1.66) Ni oxide	43.63 (1.54) oxide	66.00 (1.50) metallic
	288.22 (1.74) organic C	529.93 (1.55) Cr oxide	44.90 (2.14) oxide	68.05 (1.50) oxide
		530.94 (2.00) Cr oxide	41.97 (1.37) metallic	

Coated Inconel

The graphene-like coating was synthesized on a clean Inconel 625 sample. A freshly deposited coronene film was annealed in steps up to 350 °C. An AE spectrum from an as-synthesised coating, under UHV conditions, is presented in **Fig. 5**, and compared to the spectrum from a clean sample, the same as was presented in **Fig. 3**.

The coated Inconel 625 sample, **Fig. 5a**, shows an increase in carbon (268 eV) and oxygen (506 eV), while the intensity of signal emanating from surface metals drops relative to the spectrum from the clean sample. The increase in carbon signal results from the newly synthesized carbon-based coating and the inset in **Fig. 5a**, highlights the shape of the C KLL peak series between 242 eV and 282 eV. The C KLL peak series retains the 3-peak structure characteristic of metal carbides but the peak at 270 eV has shifted to slightly higher energy and broadened. The shift and broadening are characteristic of a graphitic carbon source, super imposed on metal carbides.²⁸

To test the permeability of the carbonaceous coating to ambient air, a coated Inconel 625 sample was exposed to ambient conditions and then re-introduced to UHV. The AES data for an air-exposed, coated sample, is included in **Fig 5b**

Figure 5: AES data: a) clean Inconel 625 (red curve) versus Inconel 625 with a graphene-like coating (green curve). The inset highlights the C KLL region. b) Inconel 625 with a graphene-like coating directly after formation in UHV (green curve) compared to the same coating after air exposure (blue curve). The insets highlight the O KLL and C KLL regions, and includes a spectrum from a pristine sample (black curve). Spectra in the C KLL region inset have been offset on the y-axis for clarity.

Fig. 5b shows that there is an increase in the oxygen level (inset 1) and a change in shape of the carbon KLL peak series (inset 2) after

air exposure. The increase in oxygen indicates that the coating does not prevent air intercalation. The change in shape of the C KLL peak series reveals a partial loss of the carbide peak structure indicating the formation of an oxide layer.

The nature of the oxide formation following air exposure was characterised by recording XPS on the air exposed graphene-like coated Inconel 625 samples, **Fig. 6**. Photoelectrons from the C1s core level can be fit, predominantly with a single peak very similar to the C1s peak in the pristine Inconel 625 sample (**Fig. 2**), but also similar to the binding energy for sp^2 C in graphene samples.^{15,36} The relative ratio between the deconvoluted peaks in the O1s core level data illustrates that Ni is now more abundant at the surface. Analysis of the metal core levels reveals that clean metal signals are still detectable at 66.00 eV and 41.97 eV for metallic Ni and Cr respectively.

Figure 6: XP spectra for a coated Inconel 625 sample after air exposure. Deconvoluted peak details are listed in Table 1.

Figure 7: A coated Inconel 625 sample. a) Optical image showing the domain-like nature of the coating. b) SEM image. An example of a coating domain has been highlighted in blue, while an example of an Inconel grain boundary has been highlighted in green. c) Representative Raman spectra from a pristine Inconel 625 sample compared to a coated sample. The

range includes the area where the D and G peaks from graphite-like materials are observed.

Despite the similarity between the photoelectron signal from the C1s core level in the pristine and coated Inconel 625 samples, microscopy images of the graphene-like coated sample reveal a completely different topography, **Fig 7**. Optical images, **Fig. 7a**, reveal that the polishing marks are no longer visible and the sample is now covered in a domain-like coating. The domains have no long-range order but appear to be regular in size, approximately 10 μm across. The SEM image in **Fig. 7b** also shows the domain-like structure of the coating. The coating domains are irregular in shape and show clear boundaries where two domains meet. The SEM image also reveals grain boundaries between grains in the underlying Inconel 625 sample, coloured as green in **Fig. 7b**. These Inconel grain boundaries are more regular in shape, with parallel sides. The coating domains appear to have formed independently, separate to the Inconel grain boundaries; the coating domains generally do not follow the substrate grain structure. A corrugated pattern is observed in the top right and bottom left of the image, indicating that in these particular domains, the coating has a corrugated surface.

To further characterise the coating, Raman spectroscopy was conducted, under ambient conditions, of both coated and pristine Inconel 625 samples, **Fig. 7c**. While the pristine sample shows little to no intensity across the spectrum range, the coated sample shows clear peaks at 1380 cm^{-1} and 1590 cm^{-1} respectively, corresponding to the D and G peaks characteristic of graphitic carbon.^{37,38} The 2D peak, usually reported between $2600 - 2900\text{ cm}^{-1}$ for graphitic samples with long range order, was not observed for either sample. The G peak results from stretching of C-C bonds in graphitic materials and can be attributed sp^2 hybridised carbon in a

honeycomb network. This justifies the use of the term “graphene-like” when describing the carbon-based coating.³⁷ The D peak is typically associated with a disorder-induced phonon mode due to crystal defects, *i.e.*, amorphous and disordered carbon bonds.³⁹ The D and G peaks in **Fig 7** are not completely separated and the D-peak can be attributed to crystallites with finite size or C-H defects in the film.^{37,40} We note that the appearance of a 2D peak in the Raman spectrum of a graphene material is often dependent on the substrate, and more specifically on the graphene-substrate interaction.³ It may be that the Inconel-coating interaction is such that the 2D peak, usually associated with graphene-like materials, is not active in this system.

The high I(D)/I(G) ratio (0.83) in the spectrum of the coated sample coupled with the observation that the two peaks are not completely separate, indicates a highly defected graphene-like coating, in keeping with the domain-like structure imaged in SEM.

The Raman spectrum of coronene is reported to consist of a dominating broad D peak and a small G peak.^{14,41,42} Therefore, from the Raman data presented here, we conclude that the thermal annealing of coronene led to a substrate-induced polymerization, which resulted in the observed graphene-like film. We note that coating attempts on pristine samples, without an initial cleaning step, did not result in a successful coating and coronene was observed to desorb without polymerizing. Hence, the substrate clearly plays a role in catalysing the low temperature graphene-growth mechanism. We note that Inconel is reported elsewhere as a suitable catalyst for the growth of carbon nanotubes.^{43,44}

The thickness of the coating was assessed by using a focussed ion beam (FIB) technique to etch a small pit in a coated region so that the cross section could be analysed. The result is presented in **Fig. 8**. An Inconel 625 sample with a graphene-like coating was first sputter coated with a thin layer of Au, followed by a thick, protective carbon layer. The protective carbon layer acts to prevent beam damage from the FIB during etching and the Au spacer allows for identification of the graphene-like coating in subsequent SEM imaging. The image in **Fig. 8** allows for immediate identification of, from bottom to top: the Inconel substrate at the bottom of the image - light grey with a sharp boundary; the Au layer - a bright horizontal band with a sharp boundary towards the graphene-like coating and a diffuse boundary towards the protective carbon layer; and that protective carbon coating - dark grey. The graphene-like coating lies sandwiched between the Inconel substrate and the Au layer, appearing as a thin dark grey line. A SEM intensity line profile, added as an inset in **Fig. 8**, gives 7 nm as an estimate of the maximum thickness of the graphene-like coating.

Figure 8: A cross-section of a coated Inconel 625 sample was obtained by focused ion beam (FIB) milling, followed by SEM imaging. The sample was coated in gold as well as a thick layer of carbon prior to FIB milling. The various layers along the cross-section are labelled. The line profile of the image intensity (inset) allows for extraction of the coating thickness.

Coating Resistance to Acid Exposure

The corrosion performance of Inconel samples was assessed by immersion in 5 wt% HCl. Representative polarization curves recorded on both pristine and coated Inconel samples after a short-term immersion of 1 day, and a coated Inconel sample after a long-term immersion lasting 40 days, are displayed in **Fig. 9a**. A Tafel analysis was performed to extract values of corrosion potential (E_c) and corrosion current density (i_{corr}), and the results are displayed in **Table 2**. The corrosion rate (CR) was obtained from the corrosion current using Faraday's Law;

$$CR = \frac{K \times E_w \times i_{corr}}{\rho}$$

Where K is the corrosion rate constant ($3272 \text{ mm} \cdot \text{A}^{-1} \cdot \text{year}^{-1} \cdot \text{cm}^{-1}$); E_w is the equivalent weight (29 g for Ni); and ρ is the density ($8.9 \text{ g} \cdot \text{cm}^{-3}$ for Ni).

In all cases, the polarization curves for coated Inconel samples are shifted to a lower i_{corr} and a higher E_c , with respect to pristine samples. The corrosion potential after 1 day of immersion increases from -308 mV for the pristine sample to 129 mV for the coated sample, **Table 2**. In addition, CR for the coated Inconel sample is 630 times lower than the CR for the pristine sample. Together, these numbers indicate that the graphene-like coating offers effective corrosion protection. Moreover, there is negligible difference between polarization curves measured for coated Inconel samples immersed for 1 day and for 40 days, indicating the long-term stability of the coating.

These results clearly prove that the graphene-like coating on Inconel samples provides both highly effective surface passivation and corrosion inhibition when immersed in 5% HCl. In addition, the 40-day immersion demonstrates that the graphene-like coating

has a high resistance to environmental degradation.

Figure 9. a) Polarization curves and b) EIS results for coated and pristine Inconel samples immersed in 5% HCl for 1 day, and a coated sample immersed for 40 days. Note the signs with squares in EIS results are Bode plots and the plots with triangles are phase diagrams. c-e) SEM images of c) pristine Inconel sample after 1 day and d) coated Inconel sample after 40 days of immersion under d) high and e) low magnification.

Table 2. The parameters resulting from Tafel fits to results following measurement of polarization curves for pristine and coated Inconel samples after immersion in 5% HCl solution.

	PRISTINE 1 DAY	COATED 1 DAY	COATED 40 DAYS
Corrosion potential (E_c , mV)	-308	129	115
Corrosion current density (i_{corr} , mA cm ⁻²)	15.60	0.025	0.030
Corrosion rate (CR, mm/year)	0.17	0.00027	0.00032

EIS measurements on both pristine and coated samples after 1 day immersion, and a coated sample after 40 days of immersion in 5% HCl are presented in **Fig. 9b** as Bode plots. At low frequencies, the impedance of coated samples is similar for the 1-day and 40-day tests at around $10^6 \Omega \cdot \text{cm}^2$, and this is

1000 times higher than the impedance of pristine Inconel at the same frequency. An analysis of the phase angle data for the pristine sample reveals two peaks, one at 100 Hz and a second at 0.01 Hz. The peak at 100 Hz is associated with capacitor-like behaviour of the native oxide on the Inconel surface. We ascribe the second peak, at 0.01

Hz, to the evolution of a double layer capacitance phenomenon at the Inconel surface following a corrosion process. Analysis of the phase angle for the coated sample reveals just one peak at 1000 Hz, and we associate this with the capacitance behaviour of the graphene-like coating on the Inconel surface.

Equivalent electrical circuit (EEC) models were produced to fit the data in **Fig. 9b** and these EEC models are shown in **Fig. 10**. In producing these models, constant phase elements were used in preference to pure capacitors. Values of capacitance were then extracted from the parameters required to describe these constant phase elements, using the Hsu and Mansfeld equation.^{45,46} The EIS fitting parameters, describing each of the circuit elements introduced to fit the data in **Fig. 9b**, are presented in **Table 3**. The model for the pristine sample and the coated samples are shown in **Fig. 10a** and **Fig. 10b** respectively. The coating shows a high resistance ($\sim 5 \text{ M}\Omega \cdot \text{cm}^2$) and low capacitance ($\sim 11 \text{ }\mu\text{S cm}^{-2}$) after both 1 day and 40 days of immersion. In contrast, the oxide layer on the pristine Inconel surface exhibits low resistance ($709 \text{ }\Omega \cdot \text{cm}^2$) and high capacitance ($114 \text{ }\mu\text{S cm}^{-2}$) values, suggesting attack of the native oxide from the electrolyte. During corrosion of the pristine sample, the charge transfer resistance is low, at $596 \text{ }\Omega \cdot \text{cm}^2$, while the double layer capacitance is high, at $24619 \text{ }\mu\text{S cm}^{-2}$. Hence, we can conclude that the pristine Inconel sample is suffering from heavy corrosion after just 1 day of immersion in 5% HCl solution.

The quality of all fits is indicated by the “goodness parameter”, and is below 1%, confirming the suitability of these models. However, close inspection of the data in **Fig. 9b** reveals an additional peak at 0.1 Hz in the phase diagram for coated samples after immersion for 40 days, compared to the

sample immersed for 1 day. An alternative EEC model is included in **Fig. 10c**, and this adapted model includes a new element in an attempt to reflect this difference in the data. We propose that this new element in the adapted model relates to the corrosion of an additional layer at the coating-metal interface. While there is a corresponding drop in the coating resistance, the resistance of this interfacial layer remains high, at about $1 \text{ M}\Omega \cdot \text{cm}^2$. Hence, the coating and this interfacial layer combine to protect the bulk Inconel sample from corrosion.

SEM images were used to assess morphology changes for pristine and coated Inconel samples after immersion in acid, **Figs. 9c-e**. The pristine sample, **Fig. 9c**, shows dark spots distributed across the image, which we interpret to represent pitting corrosion on the surface. Polishing lines are still observed, running from top to bottom in the image. The coated sample, **Figs. 9d-e**, looks decidedly different following immersion in acid. It is no longer possible to make out individual coating domains and the entire surface presents a corrugated structure, **Fig 9d**, and appears similar to the corrugated pattern discussed in relation to **Fig. 7**.

Figure 10. Equivalent electrical circuits (EEC) used for fitting EIS results of a) pristine sample at 1 day and b) coated samples at both 1 day immersion and 40 days immersion in 5% HCl and c) an adapted EEC for modelling 40 days of immersion in 5% HCl solution.

Table 3. The parameters used to produce the EEC models, fitting the EIS results for both pristine and coated Inconel samples during immersion in 5% HCl solution.

	PRISTINE 1 DAY	COATED 1 DAY	COATED 40 DAYS	COATED 40 DAYS ADAPTED MODEL
Solution resistance (R_{sol} , $\Omega \text{ cm}^2$)	1.3	1.2	1.4	1.4
Oxide resistance (R_{ox} , $\Omega \text{ cm}^2$)	709	—	—	—
Oxide capacitance (C_{ox} , $\mu\text{S cm}^2$)	114	—	—	—
Interfacial layer resistance (R_{ox} , $\Omega \text{ cm}^2$)	—	—	—	1.143×10^6
Interfacial layer capacitance (C_{ox} , $\mu\text{S cm}^2$)	—	—	—	8.42
Coating resistance (R_{coat} , $\Omega \text{ cm}^2$)	—	4.8×10^6	6.5×10^6	1.5×10^4
Coat capacitance (C_{coat} , $\mu\text{S cm}^2$)	—	11.1	11.9	41.9
Charge transfer resistance (R_{ct} , $\Omega \text{ cm}^2$)	596	—	—	—
Double layer capacitance (C_{dl} , $\mu\text{S cm}^2$)	24619	—	—	—
Goodness of Fit (%)	0.4	0.03	0.08	0.08

A Raman analysis of the coated sample after the extended 40-day acid test is shown in **Fig. 11**. The Raman analysis illustrates that the coating remains on the surface after the extended acid test with a slight improvement in the I(D)/I(G) peak ratio (0.46) for the coating when compared to the spectrum from before exposure to acid.

Figure 11: Raman spectrum from a coated Inconel sample after the 45-day acid test.

Summary

Spectroscopy evidence, in the form of Raman data, Auger spectroscopy and XPS, indicates that a graphene-like coating can be formed directly on industrially-relevant alloys at low temperatures, *i.e.*, 350 °C, much lower than what is used in standard CVD growth. Microscopy images show the coating grows to consist of flat domains, roughly 10 µm in size, joined together to form a continuous layer, up to 7 nm thick, across the substrate. Individual coating domains were observed to transverse the grains of the underlying Inconel 625 substrate. It is worth noting, however, that it was necessary to remove the native chromium oxide layer on the Inconel surface prior to coating growth.

From a comparative study between pristine and coated Inconel samples, it is shown that the graphene-like coating significantly

increases the corrosion resistance of the Inconel 625 substrate, even after 40 days of exposure to 5% HCl solution

This study provides a proof-of-concept approach toward the design of anti-corrosion graphene coatings on industrial alloys, where low temperature approaches to synthesis are paramount. There are many Ni-based alloys where the methods might be immediately transferrable and current work focuses on extending the procedures described here to non-Ni based materials. .

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Data Availability

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations.

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