

## Corrosion control: general discussion

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**Gregory Hunt** opened a general discussion of the papers by Anton Kokalj, Angelos Michaelides, and Christopher Taylor: Can you comment on how you apply DFT to non-aqueous systems (hydrocarbons)? How does the non-aqueous system influence the surface corrosion mechanism?

**Angelos Michaelides** answered: The application of a solvent to DFT can be done by co-adsorbing a very thin film of *e.g.* hydrocarbons on top of the slab and running molecular dynamics simulations. This is the so-called *ab initio* molecular dynamics approach.<sup>1</sup> We have carried out many *ab initio* molecular dynamics studies of solid-liquid interfaces, *e.g.* ref. 2 and ref. 3. Although these two papers cited deal with water/solid interfaces, the same approach can in principle be applied to liquid hydrocarbon/solid interfaces. The main and very important drawback with these approaches is their enormous computational cost and if we were to consider the solvent we wouldn't have been able to perform such an extensive set of simulations of different adsorption structures as we have shown in our paper. For complex systems like the one considered here it is probably more appropriate to study a hydrocarbon solvent with a classical method, since good parameterised force fields exist for hydrocarbon molecules.

1 R. Car and M. Parrinello, *Phys. Rev. Lett.*, 1985, **55**, 2471.

2 G. Tocci, L. Joly and A. Michaelides, *Nano Lett.*, 2014, **14**, 6872.

3 G. Tocci and A. Michaelides, *J. Phys. Chem. Lett.*, 2014, **5**, 474.

**Anton Kokalj** responded: Technically the treatment of aqueous or non-aqueous solvents is similar. This implies that non-aqueous systems can be and have been studied using DFT methods. However, I have no experience with non-aqueous systems, hence I cannot comment on your second question.

**Christopher Taylor** replied: There are two approaches that make sense. One is to use implicit solvation models where the DFT calculation is embedded in a “medium” that mimics the effect of a solvent-hydrocarbon or otherwise, and so the charges on atoms, the energies for bond-breaking, bond-making, *etc.* are modified to take into account the solvent. The second method uses “explicit solvation” and means that the DFT calculations use atomic and molecular representations of the solvent molecules and include them as either direct or indirect participants in the reaction mechanism. The surface corrosion mechanisms in hydrocarbon media will be different from those in aqueous corrosion, particularly in that they may be predominantly chemical and not electrochemical.

**Rob Lindsay** commented: Our mechanistic understanding of corrosion inhibition is still very limited. With some notable exceptions, experimental work to date has largely failed to reliably address key questions, *e.g.* coverage of inhibitor molecules required for effective inhibition. In my opinion, the three papers presented in by Anton Kokalj, Angelos Michaelides and Christopher Taylor demonstrate that cutting edge theoretical modelling is ahead of experiments in this area. Experimentalists need to catch up and provide essential data to direct further modelling work, *e.g.* identify the chemical state of the inhibited interface, so that theoreticians can undertake modelling on the most likely substrate termination.

**Alison Davenport** addressed Anton Kokalj, Angelos Michaelides and Christopher Taylor: There has been quite a bit of experimental work done on the Cu/BTA system. For example, it has been proposed by Gewirth and coworkers (*e.g.* ref. 1) that under certain conditions, inhibition is provided by a Cu(I)-BTA polymer film, which may be templated by the presence of sulphate ions adsorbed on the copper surface. It is therefore important for modellers and experimentalists to work together to ensure that the models match the experimental evidence for the nature of the system.

1 N. R. Honesty and A. A. Gewirth, *J. Raman Spectrosc.*, 2012, **43**, 46.

**Angelos Michaelides** responded: Corrosion protection provided by BTA(H) at the interface between aqueous systems and oxides is a very complex process involving a large number of factors. As computational chemists we are working to gradually increase the complexity of the system under study, in order to be able to reproduce and explain the past and current experimental work on these systems. However, we need to start from the metal/vacuum interface in order to ensure that we understand the most basic behaviour of the adsorbed molecule. So far, we find good agreement with experiments performed in these experimental conditions. We agree on the importance of experimentalists and modellers working together, and experiments performed on these less complex systems would be of great help for the early stages of the modelling work.

**Anton Kokalj** answered: I completely agree with this comment. The experimentally provided information is crucial. In particular, any atomic scale details, provided by experiments, are invaluable. Otherwise, modellers can only address some general issues on idealistic model systems, such as, low Miller index metal surfaces.

**Philippe Marcus** addressed Anton Kokalj and Angelos Michaelides: I would like to raise three points on DFT calculations on inhibitors:

- Surface reconstruction: metal surfaces can be reconstructed (e.g. Cu (111) is reconstructed under the effect of OH adsorption at high pH).
- DFT calculations on metals covered by oxide films *versus* oxides without metal underneath.
- The binding energy as an indicator of inhibitor efficiency. This is risky because a large binding energy can be associated to an adsorbed species that would promote corrosion instead of inhibition (this is the case for example for S adsorbed on different metals).

**Angelos Michaelides** responded: In our present work we were looking to study the simplest possible adsorption system for benzotriazole in order to understand its general behaviour. This means that we were working at the metal/vacuum interface where no reconstruction is expected. Further work aiming to understand this molecule should surely add a liquid interface and the related surface reconstruction of the metal. Indeed we have already started work exploring adsorption on copper oxide surfaces and are exploring the possibility of using force fields to account for a liquid film above the surface.

Regarding your second question, DFT is a costly methodology and oxides have a complex electronic structure whose study requires a larger amount of computer time than the bare metal. The first approximation to study a metal film is to model a few layers of the metal oxide only with the bottom layer of the slab fixed at the bulk positions. This should be a good enough approximation for thick enough oxide films, and indeed the literature shows that the thickness of a native film of copper oxide formed in air is a few-nm thick. For the case of a very thin film this model would probably not work and one would have to take into account the lattice mismatch with the metal and migration of electrons at the interface.

Regarding your third question, we completely agree with this statement. Surely, a “strong enough” binding energy is necessary in order to ensure that the inhibitors are competitive with corrosive molecules when adsorbing on the surface. However, this is only one of many factors which determine the effectiveness of a corrosion inhibitor and more work needs to be performed in order to identify all of them.

**Anton Kokalj** replied: Let me merge the first two questions into a single answer. The adsorption of inhibitor on non-reconstructed Cu(111)—which is the most stable among the low Miller index surfaces—and on surfaces of bulk Cu<sub>2</sub>O can be seen as the two end-member models. But actual systems relevant for corrosion, such as the reconstructed surfaces and thin oxide films supported on metals that you mentioned, may be seen to lie in between these two limits. Very thin supported oxide films indeed display very different chemical reactivity from surfaces of bulk oxides, as you showed in your recent study of Al-oxide film supported on Al.<sup>1</sup> As for the reconstructed surfaces, this is one of the reasons that, in addition to Cu(111), the adsorption was studied also on Cu(100), Cu(110), and low coordinated defects thereon. While this is not reconstruction, it may at least give an idea of the possible span of values that one may expect on more “realistic” copper surfaces. These two questions demonstrate why it is very important that experimentalists and modellers work together—as already emphasized by Alison

Davenport. Any atomic scale details that experiments can provide are invaluable for the relevant modelling.

As for the third question, I completely agree. One of the points that I make in the Conclusions of our paper is that strong inhibitor–surface bonding, as important as it may be, is by no means the only relevant factor for corrosion inhibition. Both corrosive species and inhibitors may interact strongly with the surface. So why is it that the former activate and the latter inhibit the corrosion. One answer is that corrosive species form stable soluble complexes and hence accelerate metal dissolution. In contrast, corrosion inhibitors had to form insoluble complexes (or none at all, but instead adsorb stand-alone) and thus build a protective film over metal surface. Perhaps there is a range of “good” binding energies, *i.e.*, not too weak (or the inhibitor may desorb too easily or not even adsorb) and not too strong; but I expect this to be system specific. Another factor that may be relevant, and is discussed in our paper, is the effect of inhibitor on metal work function. For further relevant factors, see also Christopher Taylor’s paper (in particular Fig. 7; DOI: 10.1039/C4FD00220B) as well as, *e.g.*, the paper of W. A. Goddard *et al.*<sup>2</sup>, who constructed a physically sound model using several different descriptors, binding energy being one among them.

1 D. Costa, T. Ribeiro, F. Mercuri, G. Pacchioni and P. Marcus, *Adv. Mater. Interfaces*, 2014, **1**, 1300072.

2 S. Ramachandran, B.-L. Tsai, M. Blanco, H. Chen, Y. Tang and W. A. Goddard, *Langmuir*, 1996, **12**, 6419–6428.

**Simon Gibbon** addressed all: Big Data is a current big push in science, seen as a grand challenge and the solution to a number of societal needs. What we have been discussing is also a grand challenge, also aligning to a number of societal needs and can certainly be enhanced by the use of Big Data. Is there an opportunity here in conjunction with the Big Data push to access significant funding to bring together all these currently disparate methodologies which are needed to address corrosion computationally?

**John Scully** responded: I agree that there is an opportunity here for corrosion. We should pay attention to developments in other fields such as health. There are challenges for the corrosion field such as a lack of data, empirical data, and issues such as “how portable” is the data? That is, should data from slightly different systems be considered in a new analysis of another condition. How do we decide what data to “include” and what data to “exclude”?

**Alison Davenport** addressed Christopher Taylor, Anton Kokalj and Angelos Michaelides: One of the most crucial events in localised corrosion is the process of repassivation, in which a surface that is dissolving suddenly starts to form a passive film and the corrosion is switched off. This implies that there is competition between dissolution and passivation on a corroding surface, and there are one or more critical factors that favour one over the other. What are the prospects for tackling this question through modelling? This will certainly be challenging since it involves the effect of an electric field at the interface as well as information on the local chemistry of the electrolyte.

**Angelos Michaelides** answered: Understanding dissolution and repassivation is a major challenge for modelling since, as already stated in the question, many factors are at play. The modelling community is working to achieve the capability of solving such complex challenges, through a number of different approaches such as multi scale methods which can combine the accuracy of quantum mechanics with the possibility of modelling larger scale systems. Moreover, enhanced sampling techniques are making it possible to understand 'rare' events such as the dissolution of a surface atom. First principles approaches are also available to explore the role of electric fields and many modellers in the electrochemistry community do such simulations already. We have for example looked at how electric fields can alter the dynamics of water molecules at surfaces<sup>1</sup> and we have also been able to explore a dissolution event purely from first principles.<sup>2</sup> With similar approaches and the multi-scale methods mentioned above, it should be possible to make more progress with our atomic level understanding of corrosion. However, in general it is true to say that relatively little is known of the atomistic details of corrosion and passivation, and simplifications are generally made when tackling these systems with modelling.

1 H. Gawronski, J. Carrasco, A. Michaelides and K. Morgenstern, *Phys. Rev. Lett.*, 2008, **101**, 136102.

2 L.-M. Liu, A. Laio and A. Michaelides, *Phys. Chem. Chem. Phys.*, 2011, **13**, 13162.

**Anton Kokalj** responded: Issues of this kind have been studied by DFT modelling (*e.g.* see the review of Maurice and Marcus<sup>1</sup> and Taylor<sup>2</sup>). Also the effect of the electric field can be and has been modelled either by charging a slab or applying a homogeneous external field perpendicular to the surface within the simulation (*e.g.*, see ref. 3 and the references therein).

1 V. Maurice and P. Marcus, *Electrochim. Acta*, 2012, **84**, 129–138.

2 C. D. Taylor, *Int. J. Corros.*, 2012, **2012**, 204640.

3 C. D. Taylor, S. A. Wasileski, J. S. Filhol and M. Neurock, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2006, **73**, 165402.

**Christopher Taylor** replied: I believe that this field is ripe for more modeling. In fact, already atomistic modeling has been applied to begin to uncover the nature of some of the fundamental processes occurring during such events. For instance, the competition between adsorption of chlorides and hydroxides on steel surfaces has been studied by Taylor,<sup>1</sup> and predictive models developed that can apply to different temperatures and chemical concentrations. The atomistic process by which chloride might displace hydroxide from a passivated nickel surface has also been studied by the Marcus group.<sup>2</sup> As more investigations of these kinds are performed, I believe we will have a fuller picture of localized corrosion and passivity, although there is much work to be done – both *in situ* experimentally and *ab initio*.

1 C. D. Taylor, *Corros. Sci.*, 2012, **68**, 591–599.

2 N. Pineau, C. Minot, V. Maurice and P. Marcus, *Electrochem. Solid-State Lett.*, 2003, **6**, B47–B51.

**Frank Renner** addressed Angelos Michaelides and Anton Kokalj: Benzotriazole or thiols are often described as corrosion inhibitors for Cu and Cu alloys. Mainly single-molecule systems are currently addressed. Do you see potential benefits for

forming stable adsorption layers by offering a multi-component system, *i.e.* for examples two molecules? I would also appreciate a response in regard of making a step towards a higher complexity of corrosion scenarios.

**Angelos Michaelides** commented in reply: It is certainly conceivable that co-adsorption of more than one inhibitor molecule could lead to interesting results. This would make a very interesting project.

We completely agree that the more realistic and complex we can make the modelling the better. In a similar manner the more well defined corrosion experiments that can be carried out, which provide precise atomic level information, the better.

**Anton Kokalj** responded: Indeed, many researchers, myself included, modelled only single-inhibitor systems. The reason is that atomistic modelling of corrosion inhibitors is at an early stage—here only studies that explicitly model pertinent interactions are meant, thus excluding numerous studies that rely on HOMO–LUMO type inferences based on inhibitor molecules alone. Mainly basic issues were studied so far, *e.g.*, how inhibitor molecules bind with metal surfaces and how this binding depends on the type of molecule, type of metal, surface terminations, and oxidation state of metal. Solvent effects on adsorption bonding were also estimated. But we have much to learn yet. As far as I know, there are many examples where multi-component systems (corrosion inhibitor formulations) display superior inhibition performance over single-component systems. Although I am ignorant of multi-component systems and how they work, I anticipate the following. There are various types of corrosion and in multi-component systems some molecules may be more effective for inhibiting one type of corrosion and other molecules more effective for inhibiting another type of corrosion. Moreover, some molecules may better inhibit cathodic and other anodic reactions. A mixture of two or more inhibitor molecules that differ in size and shape may also better tile the surface thus reducing the area of unprotected surface.

I agree that we need to make a step towards a higher complexity of corrosion scenarios.

**Simon Gibbon** continued a general discussion of the paper by Anton Kokalj: Fig. 7 in your paper shows a range of different species all following the same pattern of showing stronger adsorption on copper sites with decreasing copper co-ordination number, whether it is water, chlorine, benzotriazole or deprotonated benzotriazole. Naively, I could believe that this figure is telling us more about the chemistry of the copper surface than the adsorbing species.

Have any of your simulations shown a molecule which is more strongly bound to high co-ordination number copper sites?

For corrosion inhibition a molecule having the strongest adsorption on low co-ordination number sites (defects) is required. For lubrication the opposite is true, where the molecule needs to preferentially adsorb to high co-ordination number sites (flat surfaces). If such molecular specificity/separation did not occur in practice in systems formulated for both lubrication and inhibition, then multi-layer structures would be required.

Is the DFT approach also able to help me select a lubricant molecule?

**Anton Kokalj** answered: I would say that Fig. 2 of our paper is telling us about the chemistry of both involved constituents, that is, adsorbate and copper surface. That the molecule–surface bonding becomes stronger on passing from densely packaged Cu(111) to low coordinated surface defects is not surprising for late-transition metal surfaces. This can be rationalized in terms of the Hammer–Nørskov chemisorption model,<sup>1</sup> where the d-band center is a principal descriptor, *i.e.*, the metal d-band center upshifts as the coordination decreases which in turn results in stronger bonding. However, not all presented species follow the same trend: atomic H is rather insensitive to surface details and the physisorption modes are less sensitive to surface details than chemisorption modes. Among the presented species deprotonated benzotriazole (BTA) displays the strongest dependence on the coordination of copper atoms.

As for the inhibitor/lubricant issue, I believe that the requirement that lubricant should bind stronger to flat facets than defects is too strong. Adsorption of inhibitor at low coordinated defects and lubricant at flat facets can be achieved even if the lubricant prefers the defect sites. What is required is that the lubricant displays a weaker preference to defect sites than the inhibitor. Let me make a detour to heterogeneous catalysis as to make a supporting example: recently we studied a co-adsorption of ethylene and CO on stepped Cu(410).<sup>2</sup> The CO shows a much weaker dependence on the copper coordination number than ethylene and only marginally favors the step-edge over the flat facets. As a result, ethylene is adsorbed at step-edges and CO at terraces. This was experimentally verified.

Furthermore, in a recent study of adsorption of several azoles (among them also mercapto-azoles) on copper surfaces,<sup>3</sup> we found that molecular bonding *via* S is much less sensitive to surface details than the molecular bonding *via* N. Indeed, the N heteroatom is particularly sensitive to surface details. This, together with your premise that lubricant should adsorb on flat facets, suggests that N is not a good heteroatom for lubricant, and S would be better.

DFT is a very good tool to understand such type of bonding issues. But DFT has also been used to model other relevant aspects of a lubricant, such as friction.

1 B. Hammer and J. K. Nørskov, *Adv. Catal.*, 2000, **45**, 71–129.

2 T. Makino, M. Okada and A. Kokalj, *J. Phys. Chem. C*, 2014, **118**, 27436–27448.

3 N. Kovačević, I. Milošev and A. Kokalj, *Corros. Sci.*, 2015, doi:10.1016/j.corsci.2015.05.041.

**John Scully** asked: So what would a bad inhibitor “look like” in terms of the parameters that you modeled? What are the features of a bad inhibitor in contrast with a good inhibitor for corrosion? How does the corrosion field sort out the plethora of inhibitors using these modeling advances? Would one factor be poor adsorption relative to water and/or chloride?

**Anton Kokalj** replied: To the last question, concerning the “poor” adsorption, I answer affirmatively.

Molecular modelling of corrosion inhibitors has indeed become very fashionable in corrosion inhibition studies and a quick literature search reveals that in the last decade the number of such studies increased rapidly. By far the prevalent approach in the literature is based on considering only inhibitor molecules and making HOMO–LUMO type inferences. I don't believe this approach is very useful, *i.e.*, it is a kind of black-box.<sup>1</sup> I completely agree with the

statement made recently by Robert Lindsay *et al.* that “in terms of predictive power, such an approach has at best limited value, and is potentially simply misleading”.<sup>2</sup> A step forward is to rigorously model interactions between components of corrosion system and recently several attempts in this direction appeared. In such studies the most utilized descriptor is the molecule–surface binding energy, typically calculated at metal/vacuum interface. While this parameter is likely important, it is nevertheless only one among the relevant factors. Aqueous-phase adsorption energy is a more relevant parameter, but harder to calculate. For example, a given molecule may form a strong adsorption bond and also hydrates strongly: if the latter is stronger than the former the molecule may not even adsorb (that would be a bad inhibitor). Hence the solubility should be neither too large nor so weak as to make an inhibitor insoluble. A given reactive molecule may display (i) strong adsorption bonding, (ii) strong hydration as well as well as (iii) the ability to form soluble molecule–metal complexes. So it is the “differential” bonding that matters, *i.e.*, a good inhibitor molecule should favour (i) over (ii) and disfavour (iii). But such “differential” interplays are much harder to anticipate and ascertain, because they depend on “details”. Furthermore, a good inhibitor should have a higher affinity towards under-coordinated defect sites than corrosive species; *e.g.*, metal dissolution likely proceeds *via* kink sites, hence an inhibitor should “protect” them. Another way the inhibitor molecule may act against corrosion is *via* some non-steric inductive or indirect effects, *e.g.*, the adsorption of an inhibitor may affect not only adsorption sites but also neighbouring sites, which become less susceptible to corrosion reaction.<sup>3</sup> A non-local factor of this type that may be relevant, and is discussed in our paper, is the effect of an inhibitor on the metal work function; adsorption of benzotriazole considerably reduces the work function of copper. Although under realistic conditions several factors would counteract the work function change, some effect may still survive. The reduction of the metal work function should make anodic reaction less favourable and *vice versa* for cathodic reaction. Hence this effect is a “double-edged sword”, depending on which reaction is rate limiting. These are some hints on parameters that a good inhibitor should display (and *vice versa* for a bad inhibitor), some of which were considered in the paper. But I believe that these alone are insufficient to be predictive. Much work needs to be done in this direction. In this respect the general comment made by Robert Lindsay that “our mechanistic understanding of corrosion inhibition is still very limited” is right on target.

Last but not the least, it should be noted that atomic-scale models represent only a part of the whole picture. I agree with Christopher Taylor, who argued in his presentation, that predictive models will need to address phenomena on different length (and time) scales (DOI: 10.1039/C4FD00220B).

1 A. Kokalj, *Electrochim. Acta*, 2010, **56**, 745–755.

2 P. Morales-Gil, M. Walczak, R. Cottis, J. Romero and R. Lindsay, *Corros. Sci.*, 2014, **85**, 109–114.

3 P. Kutej, J. Vosta, J. Pancir, J. Macak and N. Hackerman, *J. Electrochem. Soc.*, 1995, **142**, 829–834.

**Stuart Lyon** enquired: The calculations refer to adsorption from vacuum. How could this approach be modified to a technically important aqueous system?



**Anton Kokalj** replied: The majority of calculations indeed refers to adsorption from vacuum. The reason for this is that vacuum calculations are both conceptually as well as technically simpler. In a reductionistic manner one first starts with a simpler system and elaborates later. For example, adsorption from an aqueous system is due to an interplay of several competitive effects, *i.e.*, molecule–surface, molecule–water, and surface–water interactions. Hence, it is important to understand the individual effects in order to interpret the numbers that result from sophisticated simulations. In Section 3.2 of our paper, the influence of the solvent is roughly estimated using the implicit solvent model and thermodynamic cycle. The use of the latter enables the understanding of individual involved effects. A more sophisticated approach would be to treat the solvent explicitly atom by atom; its liquid character is then modelled by performing molecular dynamics simulations. The third option for modelling aqueous systems is a hybrid approach where several water molecules are treated explicitly and the rest of the solvent implicitly.

**Mira Todorova** commented: 1) I am not sure whether I completely understand which quantities within the thermodynamic cycle (Scheme 3, p. 11 of your paper) were obtained by density-functional theory calculations and how the calculations were performed. This relates in particular to the  $\Delta\Delta G_{\text{solv}}$  term appearing in eqn. 4 and 5 of your paper. Were the terms related to this formula actually calculated by performing explicit calculations for a “surface/water” and a “surface/adsorbate/water” supercell (maybe by using an implicit water *via* some solvation model, rather than explicit water) or are these components within the thermodynamic cycle approximated by the calculated binding energy  $E_{\text{B}}^{\ominus}$ ? Are the used EA (electron affinities) taken from thermodynamic tables?

2) Concerning the  $\text{CuO}_2$  system: what is your opinion on how important the correct description of the band gap is in the context of the adsorption studies?

**Anton Kokalj** answered: Almost all quantities in eqn. 4 and 5 were obtained with DFT calculations. The only exception is the work function of the metal/water/vacuum system ( $\Phi^*$ , eqn. 6), where the experimental values were taken for  $\Delta\Phi$ ;<sup>1</sup>  $\Delta\Phi$  is a variation of the metal work function due to a thick layer of liquid water (for more details, see the footnote § in the paper). All solvation terms were calculated with an implicit solvent model (for more details see the ESI of ref. 2 and 3), whereas for Fig. 6 the dependence of the  $\Delta\Delta G_{\text{solv}}$  terms of metal slabs on the electric field (eqn. 9) were estimated from the behaviour of adsorbed H-up and H-down water bilayers on the applied electric field (see the ESI of ref. 2).

Electron affinities were calculated as the difference between total energies of neutral and anionic forms ( $E_{\text{X}} - E_{\text{X}^-}$ ) as obtained by molecular calculations using local Gaussian-type orbital basis set. BTA and Cl have positive electron affinities: PBE calculated values are 3.53 and 3.69 eV, respectively, whereas the experimental value for Cl is 3.62 eV. (Even for molecules with negative electron affinities, pragmatic DFT calculations using small local basis sets often give reasonable results.<sup>4</sup>)

The issue of the band gap of  $\text{Cu}_2\text{O}$  is certainly important and indeed plain GGA functionals considerably underestimate it (PBE gives 0.41 eV, whereas the experimental value is 2.14 eV). In your paper (DOI: 10.1039/C4FD00238E) you stated that defect formation energies calculated with plain GGA functionals can

be way off (I've encountered similar problems in studies of Li-ion battery materials, where the +U correction is needed to remedy the situation). But I would anticipate that correct description of band gap is less important for adsorption studies than for defect formation energies and other issues where band alignment is crucial. Furthermore, it is reasonable to assume that adsorption trends turn out better than individual adsorption energies (and in the paper the emphasis is on the trends). The adsorption of benzotriazole was studied in considerably less detail on Cu<sub>2</sub>O than on Cu surfaces and one among future improvements of the Cu<sub>2</sub>O model is to take the issue of the band gap into account either with the +U correction or by using hybrid functionals. This would quantify how important the issue of the band gap is, in the context of adsorption of the inhibitor.

- 1 S. Trasatti and L. M. Doubova, *J. Chem. Soc., Faraday Trans.*, 1995, **91**, 3311–3325.
- 2 A. Kokalj, S. Peljhan, M. Finšgar and I. Milošev, *J. Am. Chem. Soc.*, 2010, **132**, 16657–16668.
- 3 S. Peljhan, J. Koller and A. Kokalj, *J. Phys. Chem. C*, 2014, **118**, 933–943.
- 4 M. C. Kim, E. Sim and K. Burke, *J. Chem. Phys.*, 2011, **134**, 171103.

**Gerald Frankel** communicated: It has been shown that BTA is more effective on Cu<sub>2</sub>O than on bare metal or CuO. In fact, there seems to be some specificity of BTA for systems that form monovalent ions. For example, it is very effective for Ag, but not for Fe. You did not present results for CuO, but did show a figure comparing Cu and Cu<sub>2</sub>O. The binding energy was stronger for Cu than for Cu<sub>2</sub>O. Is there anything in your calculations that might explain this behavior of BTA? It might be useful both in validating your results and for providing a basis for the development of new inhibitors.

**Anton Kokalj** communicated in response: This is a very good point, *i.e.*, the specificity of BTA for systems that form monovalent ions. Unfortunately, we haven't looked at that yet. What I do know is the following: calculations indeed suggest that the bonding of deprotonated BTA is stronger to Cu than Cu<sub>2</sub>O surfaces. Also the BTAH<sub>(ads)</sub> → BTA<sub>(ads)</sub> + H<sub>(ads)</sub> dissociation is more favourable on the former (exception to this are hydroxylated Cu<sub>2</sub>O surfaces). The pH is likely important here: at higher pH, copper surfaces are oxidized and solvated benzotriazole exists in deprotonated BTA<sup>−</sup> form (its pK<sub>a</sub> constant is about 8), whereas at lower pH the situation is the opposite (reduced copper surfaces and neutral BTAH form). But only deprotonated BTA bonds strongly to the surfaces of copper! This may perhaps explain the relevance of Cu<sub>2</sub>O. As for the bonding to Fe systems, it should be noted that benzotriazole bonds differently to Cu and Fe surfaces.<sup>1</sup> While Cu and Ag are not reactive enough to interact with the benzotriazole's π-system (Cu can do it only as an exception and even then the interaction is driven by the dispersion van der Waals forces), Fe can readily do so. Hence benzotriazole binds to Cu (and Ag) surfaces predominantly *via* σ-bonding and to Fe surfaces predominantly *via* its π-system. This implies different adsorption geometries of benzotriazole on Cu and Fe surfaces, which in turn entails different adsorption induced work function changes on the two metals.

- 1 N. Kovačević and A. Kokalj, *Mater. Chem. Phys.*, 2012, **137**, 331–339.

**Vincent Maurice** communicated to Anton Kokalj and Angelos Michaelides: One of the aspects discussed to evaluate the corrosion inhibition efficiency was the bond strength. However, some elements known as very detrimental to the corrosion resistance such as Cl and S also bond strongly to metallic surfaces and I agree that the adsorbate bond strength is a good criterion to discuss competitive adsorption. However, one secondary effect of strong adsorbate bonding is weakening of the bond strength of the metallic atoms which are nearest neighbours to the ones directly bonded to the adsorbate. As a result, metal dissolution is promoted in the presence of adlayers of elements such as Cl and S, as shown in previous studies.<sup>1–3</sup> Could you speculate on the implication for the mechanism of inhibition if the inhibitor is strongly bonded?

1 P. Marcus and J. Oudar, *Appl. Surf. Sci.*, 1979, **3**, 48–67.

2 S. Ando, T. Suzuki and K. Itaya, *J. Electroanal. Chem.*, 1996, **412**, 139–146.

3 O. M. Magnussen, L. Zitzler, B. Gleich, M. R. Vogt and R. J. Behm, *Electrochim. Acta*, 2001, **46**, 3725–3733.

**Angelos Michaelides** communicated in reply: It is not clear yet when a strongly bound molecule results in a good or bad inhibitor. We have verified with the benzotriazole systems, especially those presenting adatoms that chelation is not likely, since it requires a large amount of energy (over 5 eV) to remove a molecule/adatom complex from the surface. More comparative work is needed between strongly bound molecules which are good and bad inhibitors in order to be able to tell if there is an *a priori* way of assessing when a strongly bound molecule will result in the dissolution of the surface.

**Anton Kokalj** communicated in response: I completely agree with this comment. As already mentioned in the answer to Philippe Marcus' question, the pertinent difference between corrosive species, such as Cl and S, and corrosion inhibitor might be that the former form soluble and the latter insoluble complexes. The first thus promote the metal dissolution, whereas the later forms a protective insoluble film on the metal surface.

I anticipate two factors that may be relevant in this respect. The first is whether the formed complexes are charged or neutral: the former hydrate strongly and would be soluble and the latter hydrate weakly and would be insoluble. The second factor is related to molecular size: *e.g.*, the Cl<sup>−</sup> is smaller than BTA<sup>−</sup>, which is why the former hydrates stronger. Analogously, the CuCl<sub>2</sub><sup>−</sup> complex is much smaller and more soluble than [BTA<sub>x</sub>–Cu<sub>y</sub>]<sup>δ±</sup> complexes (for generality let us assume that the complex may be non-stoichiometric and thus charged).

**Vincent Maurice** further communicated: The weaker efficiency of benzotriazole at acidic pH is discussed in terms of weaker adsorption of the molecule in the hydrogenated form (BTAH). However, copper dissolves at acidic pH with Cu adatoms available for forming BTA–Cu complexes which might be more relevant to discuss.

**Anton Kokalj** communicated in reply: Although at acidic pH Cu ions are available, the benzotriazole is in neutral BTAH form. But for the formation of BTA–Cu complexes, the BTA form (*i.e.* benzotriazole stripped from its H1 atom/

proton) is needed. Hence there are pros and cons. Nevertheless, this is a useful suggestion that should be considered.

That the argument of the weaker adsorption of BTAH seems relevant is corroborated by the fact that 1-methyl-benzotriazole is not effective in preventing Cu corrosion, because the substitution of the H1 atom by a methyl group prevents the formation of BTA. This strongly suggests that benzotriazole is active against corrosion in the BTA form, which binds strongly.

**Tom Majchrowski** communicated: In the proposed DFT calculations, how would the presence of alloying additions alter the adsorption of the benzotriazole, would there be a competitive effect observed? Also, what is the effect of the interactions of the adsorbed species?

**Anton Kokalj** communicated in response: This is a very interesting question. Benzotriazole interacts differently with different metals, *e.g.*, it forms a stronger chemisorption bond to transition metals with an open d-band than to transition metals with a fully occupied d-band. On transition metals with an open d-band, the inhibitor prefers to chemisorb parallel to the surface with a pronounced  $\pi$ -d hybridization, whereas on transition metals with fully occupied d-band and on sp-metals, benzotriazole prefers to chemisorb through  $\sigma$ -molecular orbitals.<sup>1</sup> Hence benzotriazole would bind differently to copper than to alloying additions, but specifics depend on the actual alloy system.

As for the second question, I am not sure I understand what you meant by “the effect of the interactions of the adsorbed species”, hence I will assume that you meant the lateral interactions between adsorbates. Benzotriazole displays a rich variety of lateral interactions. First, there are long range lateral dipole–dipole interactions due to a large permanent dipole moment of benzotriazole (4.1 D). These are repulsive for perpendicular BTAH adsorption modes and slightly attractive for parallel BTAH adsorption modes; this behaviour is due to orientation of molecular dipole in the adsorbed state. For deprotonated BTA, these dipolar interactions are far less important due to considerable adsorption induced charge transfer, which greatly reduces the dipole. At higher coverage (say, intermolecular distances shorter than about 5 Å) the lateral van der Waals dispersion interactions become important (see ref. 2 and 10.1039/C4FD00273C); these are always attractive. At short intermolecular distances, properly oriented BTAH molecules also form intermolecular N1–H $\cdots$ N hydrogen bonds. And at even higher coverage Pauli repulsion occurs due to steric hindrance (molecular overlap). The presence of water solvent affects the lateral interactions, in particular water molecules screen the long range dipole–dipole interactions and diminish the “importance” of intermolecular BTAH–BTAH hydrogen bonding, because water molecules can also form hydrogen bonds with BTAH molecules.<sup>3</sup>

1 N. Kovačević and A. Kokalj, *Mater. Chem. Phys.*, 2012, **137**, 331–339.

2 A. Kokalj, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2011, **84**, 045418.

3 A. Kokalj, S. Peljhan, M. Finšgar and I. Milošev, *J. Am. Chem. Soc.*, 2010, **132**, 16657–16668.

**Gregory Hunt** communicated: How do you use Fig. 2 in your paper to select corrosion inhibitors? How would a non-aqueous system affect your conclusions?

**Anton Kokalj** communicated in reply: I do not think that Fig. 2 can be used to select corrosion inhibitors. Only one inhibitor (benzotriazole) along with some other species (Cl, H, H<sub>2</sub>O) are considered therein. Nevertheless, Fig. 2 tells something important, *i.e.*, benzotriazole displays the largest bonding enhancement on passing from densely packed Cu(111) to low-coordinated defects among the presented species, which indicates its ability to passivate reactive under-coordinated surface sites. This bonding enhancement is also a thermodynamic driving force for the formation of the BTA–Cu organometallic complexes; according to experimental evidence the ability of benzotriazole to inhibit corrosion is due to the formation of these complexes.

As for the second question, I will instead comment how aqueous solvent affects the results of Fig. 2, because I do not have experience with non-aqueous solvents. The presence of a solvent considerably reduces the magnitude of adsorption energies. This is because in vacuum non-dissociative adsorption can be described solely as bond-making, whereas in a solvent phase it consists of bond-breaking and bond-making. Namely, prior to adsorption the molecule must get rid, at least partially, of its solvation shell and must also empty adsorption site by displacing solvent molecule(s) from the surface; this is bond-breaking and costs energy. Only then the adsorption bond can form (energy gain). Fig. 2 shows that in vacuum Cl binds stronger to Cu surfaces than standalone BTA, but in an aqueous solvent the just mentioned bond-breaking effects reverse the trend, because Cl<sup>−</sup> is much smaller than BTA<sup>−</sup> and hydrates by about 0.6 eV stronger. The solvent also diminishes adsorption energy dependence on the coordination of surface metal atoms because the adsorbate has to displace solvent molecule(s) from the surface during specific adsorption and a water molecule displays a similar bonding enhancement trend (although less pronounced) as benzotriazole and Cl.

How the non-aqueous solvent affects the results depends on the solvent characteristics. Yet some of the above explained effects may still be relevant, in particular for polar solvents.

**Simon Gibbon** continued a general discussion of the paper by Angelos Michaelides: How would you select the best corrosion inhibiting molecule?

**Angelos Michaelides** answered: Unfortunately it is not completely clear yet what makes for an effective corrosion inhibitor. Compared to fields like chemical catalysis (see *e.g.* ref. 1) our understanding of what the molecular level “descriptors” are of a good corrosion inhibitor have yet to be identified. However, a few factors are likely to contribute: molecules which bind strongly to the surface and form uniform overlayers are good candidates. Crucially though further computational and experimental work is needed on well defined model systems in order to identify all the factors which contribute to good inhibition efficiency.

1 A. Michaelides, Z.-P. Liu, C. J. Zhang, A. Alavi, D. A. King and P. Hu, *J. Am. Chem. Soc.*, 2003, **125**, 3704.

**Anton Kokalj** commented: For the time being, I would heavily rely on a “guided” experimental trial-and-error approach. Only experiments can tell whether a given molecule is a good inhibitor for a given application. I don’t

believe the corrosion inhibitor modelling has already reached the predictive stage (but we are moving forward toward this goal). Nevertheless, modelling can provide some useful hints and insights. This means that the above mentioned trial-and-error approach would not be completely blind but would be driven, not only by researcher's knowledge and chemical intuition, but also by insights gained by modelling. In order to select a good inhibitor for a given application, I would pursue a "learning" iterative approach of experiments and modelling, where each new iteration bases on the knowledge gained in previous iteration(s).

**Christopher Taylor** added to the previous replies: I propose in my paper that first a model be developed that describes the key phenomena controlling the inhibitor performance. The next step would be to couple this model with a "design tool", that takes a class of molecules, perhaps broken into fragments (head, tail, substituent, for example) and begins to iteratively compute the anticipated performance using this inhibition model. The design tool would employ a "machine learning" strategy to mix and match different head/tail/substituent combinations in order to arrive at the best inhibitor. Some additional chemistry modules should probably be included to screen out combinations that would be expected to be too difficult/expensive to synthesize or those that may be environmentally toxic, for example. Cheminformatics tools can be coupled in to perform these last couple of functions, and perhaps other aspects of the model that were addressed in the paper.

**Mira Todorova** said: 1) Four different van-der-Waals functionals are tested in this work. With respect to their construction the D2 and the TS can be considered to be empirical (in the sense, that they present a correction to the calculated energy, but are not contained within the xc-functional), while the vdW-contribution within the other two functionals is contained within the xc-functional term. There are several instances within your paper, where significant differences in the description of the studied system are observed, depending on which functional is used. For example:

- the energy range found for the adsorption of the 'flat' BTAH geometry, which is almost doubled by using vdW-TS ( $-1.29$  eV) compared to the  $-0.66$  eV of vdW-DF (page 7).
- the comment on page 9 which states that vdW-DF usually under-binds while vdW-TS and vdW-D2 usually over-bind.

Can you comment on what features of these four functionals are responsible for such differences in performance? Should one expect in general a better description when using the optB86b-vdW functional?

2) In Section 4.1, where the adsorption behaviour of BTA is examined, it is suggested that BTAH undergoes "dehydrogenation" rather than "deprotonation". Wouldn't you expect this to be different (the opposite) in the presence of water?

**Angelos Michaelides** answered: This is an interesting and important question. The short but not very deep answer is that the performance of DFT xc-functionals depends on a balance of the exchange and correlation terms. For a fuller answer that goes into the details, including several of the functionals considered in our article, we have recently written a review article: see ref. 1. The optB86b-vdW functional and the related optB88-vdW and optPBE-vdW functionals<sup>2</sup> were

developed based on the realisation that the exchange component used in the original Dion *et al.* functional<sup>3</sup> was too repulsive which very often leads to underbinding. This underbinding is largely cured in the modified vdW-DFs and for a broad range of systems we do see excellent performance with these functionals, *e.g.* solids and ice,<sup>4–6</sup> adsorption.<sup>7,8</sup> However all functionals have problems and weaknesses in certain areas and for some adsorption systems we see overbinding with our revised vdW-DFs (*e.g.* water on h-BN)<sup>9</sup>. So the answer to the question is that yes, optB86b-vdW is in this system likely to be performing the best out of those considered, but in general, one must be careful and critical when discussing adsorption energies. Yes, if liquid water was present there is certainly the possibility (depending on the precise conditions) that deprotonation rather than dehydrogenation would be observed.

- 1 J. Klimeš and A. Michaelides, *J. Chem. Phys.*, 2012, **137**, 120901.
- 2 J. Klimeš, D. R. Bowler and A. Michaelides, *J. Phys.: Condens. Matter*, 2010, **22**, 022201.
- 3 M. Dion, H. Rydberg, E. Schröder, D. C. Langreth and B. I. Lundqvist, *Phys. Rev. Lett.*, 2004, **92**, 246401.
- 4 J. Klimeš, D. R. Bowler and A. Michaelides, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2011, **83**, 195131.
- 5 G. Graziano, J. Klimeš, F. Fernandez-Alonso and A. Michaelides, *J. Phys.: Condens. Matter*, 2012, **24**, 424216.
- 6 B. Santra, J. Klimeš, A. Tkatchenko, D. Alfè, B. Slater, A. Michaelides, R. Car and M. Scheffler, *J. Chem. Phys.*, 2013, **139**, 154702.
- 7 J. Carrasco, B. Santra, J. Klimeš and A. Michaelides, *Phys. Rev. Lett.*, 2011, **106**, 026101.
- 8 J. Carrasco, W. Liu, A. Michaelides and A. Tkatchenko, *J. Chem. Phys.*, 2014, **140**, 084704.
- 9 Y. S. Al-Hamdani, M. Ma, D. Alfè, O. A. von Lilienfeld and A. Michaelides, *J. Chem. Phys.*, 2015, **142**, 181101.

**Su-Ting Cheng** asked a follow up question to MiraTodorova's question for Angelos Michaelides: It is interesting to see that the van der Waals correction can change the adsorption geometry to this extent. The hydrogen bonding is shown to be crucial in this system. Another example for hydrogen bonding being deterministic would be probably water, which could be also the solvent for BTAH. I am curious, could the adsorption geometry be altered again or changed drastically, with the presence of water molecules (the solvent) in the calculation?

**Angelos Michaelides** replied: This is an interesting question but we haven't looked at water adsorption along with BTAH or BTA on Cu, so we don't know the impact it will have.

**Anton Kokalj** commented: I find the change of adsorption geometry due to inclusion of van der Waals (vdW) correction both intuitive and expected. I guess the most interesting issue in this respect is the emergence of stable tilted adsorption modes. This can be rationalized as follows: dispersion interactions prefer to maximize molecular contact with the surface, thus favouring the parallel adsorption mode. However, chemisorption bonding *via*  $\sigma$  molecular orbitals favours the upright bonding. Yet we have shown in ref. 1 that tilting of an upright BTAH molecule is extremely soft even without the vdW correction, *i.e.*, there is almost no energy penalty up to 20° tilt, whereas the penalty for 45° tilt is mere 0.08 eV (PBE data). But at such large tilt there is a gain due to dispersion vdW interaction, which further increases the tilt. Hence the tilted structure is a compromise

between the upright structure favoured by chemisorption and parallel structure favoured by dispersion interactions.

As for the effect of solvent water molecules on the hydrogen bonding between BTAH molecules, you are certainly right. Water molecules can form hydrogen bonds with BTAH and thus diminish the “importance” of BTAH–BTAH hydrogen bonding. However, the BTAH–BTAH hydrogen bonds are stronger than the BTAH–H<sub>2</sub>O bonds. Hence, the net effect of hydrogen bonding stabilization is reduced from 0.5 eV/molecule in the gas-phase to about 0.1 eV/molecule in the aqueous phase, as deduced from approximate calculations.<sup>2</sup>

1 S. Peljhan and A. Kokalj, *Phys. Chem. Chem. Phys.*, 2011, **13**, 20408–20417.

2 A. Kokalj, S. Peljhan, M. Finšgar and I. Milošev, *J. Am. Chem. Soc.*, 2010, **132**, 16657–16668.

**Clara Wren** enquired: The DFT calculations which investigate the stability of one single molecule on alloy slabs are not very useful. Have you expanded your calculations to benzotriazole–(H<sub>2</sub>O)<sub>n</sub> cluster systems? Will this change the bond energy or van der Waals energy? The dipole moments of the water molecules can influence the Coulombic interaction. How do you incorporate this effect in your DFT calculations?

**Angelos Michaelides** replied: In our paper we report results for single molecules and overlayers of molecules on the surface. It is not restricted to single molecules – please consult the paper. We do not show results for any alloy surfaces, our study focuses on copper. Again please consult the paper on this point. Even if our paper was restricted to single molecules, it would still be of value as this is surely the first step in understanding any adsorption system.

We have not looked at BTAH–water complexes and so cannot comment on this. It would be interesting and nice to explore this in the future. We have, however, extensively looked at water adsorption on surfaces, see. *e.g.* ref. 1.

DFT is an electronic structure technique that explicitly captures (from the electron density) dipolar and Coulombic interactions. For an introduction to DFT approaches see some recent reviews in the *Journal of Chemical Physics*.<sup>2–4</sup>

1 J. Carrasco, A. Hodgson and A. Michaelides, *Nat. Mater.*, 2012, **11**, 667.

2 K. Burke, *J. Chem. Phys.*, 2012, **136**, 150901.

3 A. Michaelides and J. Klimeš, *J. Chem. Phys.*, 2012, **137**, 120901.

4 A. D. Becke, *J. Chem. Phys.*, 2014, **140**, 18A301.

**Anton Kokalj** replied: The adsorption of benzotriazole was modelled also at the metal/water interface. The corresponding modelling is, however, not trivial and the effect of water was only roughly estimated using the implicit solvent model (see Section 3.2 in our paper). Indeed, the presence of aqueous solvent considerably affects the energetics of adsorption due to an interplay of several competitive effects, *i.e.*, molecule–metal, molecule–water, and metal–water interactions. Consequently, the net adsorption energies are much reduced in the aqueous phase with respect to the gas-phase.

The dipole moment of water indeed influences Coulombic interactions. For example, water molecules screen the long range lateral dipole–dipole interactions between adsorbed molecules (an estimate is shown by a thin dash-dotted line in Fig. 4 in our paper). Coulombic interactions are treated naturally in DFT



calculations. This is true even when the solvent is present, provided that the model is sophisticated enough.

**Simon Gibbon** addressed Angelos Michaelides and Anton Kokalj: If my understanding is correct, your two papers have used different approaches to studying the effect of copper co-ordination on the interaction of benzotriazole with a copper surface, is this correct and has it resulted in differences in your results?

**Angelos Michaelides** responded: Both papers studied the adsorption behaviour of benzotriazole (BTAH) on copper surfaces using density functional theory (DFT). In DFT an appropriate “functional” needs to be chosen, and the choice of functional can determine the adsorption configurations obtained (see. *e.g.* ref. 1). In the two papers different functionals were chosen: we used a self-consistent van der Waals-inclusive functional,<sup>2</sup> while in the other paper a combination of an empirical van der Waals-inclusive functional and other functionals which do not account for dispersion interactions were used. While we obtained some differences in the results, the overall picture on the behaviour of BTAH is consistent in the two studies.

1 J. Klimeš and A. Michaelides, *J. Chem. Phys.*, 2012, **137**, 120901.

2 J. Klimeš, D. R. Bowler and A. Michaelides, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2011, **83**, 195131.

**Anton Kokalj** answered: The approaches in the two papers are rather similar, but the focus is to some extent different. Gattinoni and Michaelides (10.1039/C4FD00273C) studied the adsorption of benzotriazole on Cu(111) and also the BTA–Cu organometallic complexes on Cu(111)—by “complex” I mean that BTA molecules are linked *via* Cu atoms (ions) that are extraneous to the copper lattice—whereas I presented the adsorption on Cu(111), Cu(100), Cu(110) and low coordinated defects thereon as well as on several surfaces of Cu<sub>2</sub>O, including the BTA–Cu complexes.

Perhaps, the largest difference between the two studies is the use of different functionals. Gattinoni and Michaelides used the optB86b-vdW, whereas I used the PBE for upright adsorption modes (chemisorption) and PBE-D' for parallel adsorption modes (physisorption); PBE-D' includes a Grimme's empirical van der Waals correction, reparametrized to reproduce experimental adsorption energy of benzene on Cu(111). Due to the use of different functionals there are, of course, quantitative differences. But qualitatively the results of the two papers are compatible. For example, both show that (i) benzotriazole displays reach chemistry on Cu surfaces, (ii) dissociated BTA bonds considerably stronger than neutral BTAH, and that (iii) the bonding of BTA is even stronger in the BTA–Cu organometallic complexes. Another difference is that Gattinoni and Michaelides focused on high-coverage BTAH phases, whereas I focused on long range dipole–dipole interactions between BTAH at lower coverage.

**Vincent Maurice** communicated: In the discussion of the BTA inhibition in alkaline solution, the presence of the copper surface oxide should be taken into account.

**Angelos Michaelides** communicated in reply: In the study of the interaction of BTA with copper we have started with the simplest possible system in order to obtain a general understanding of the adsorption behaviour of the molecule. Doing so also allows us to compare with well defined surface science experiments performed under the same conditions. A more complex system, such as a BTA/oxide system, certainly needs to be studied and we are working on this at the moment. As modellers, we welcome any input from experimentalists regarding the fundamental aspects of the corrosion process that need to be taken into account.

**Clara Wren** continued a general discussion of the paper by Christopher Taylor: You mentioned that you have expanded your calculations to investigate clusters using molecular dynamic simulations. In your MD calculations, how large was the size of the clusters in your unit cell, and how many unit cells were considered? How do the size of the cluster and the optimum size of the calculation matrix affect the bonding energy and the corrosion inhibition behaviour of, for example, benzotriazole?

**Christopher Taylor** replied: Using classical molecular dynamics around 10 000 molecules can be simulated on a single multi-core desktop PC. This enables larger diversity of molecular arrangements and solvation environments to be studied. When the simulations become more complex than, say, the DFT models of single molecules on clean surfaces, it is important to apply statistical sampling to get an average picture of the behavior of inhibitor self-assembled monolayers, their structure, and their ability to protect the surface against corrosion. These studies are in progress, so I do not have conclusive answers to your questions as yet.

**David Shoesmith** said: We have tried many modelling approaches to model/ assess fuel wastefrom and nuclear waste container corrosion ranging from deterministic models to Monte Carlo simulations but have not found a method to interlink them sensibly without extreme complexity. You appear to have a format for interlinking these approaches. Can you discuss how close to such a synthesis you are?

**Christopher Taylor** answered: The formation of a “multiscale model” is often complex as you mention. The model developed for inhibitors has addressed several factors, but is still far from a complete integration. The current model combines thermodynamic quantities – for inhibitor speciation and partitioning, and the formation of self-adsorbed monolayers – with kinetic terms for the corrosion rates. Some of the pieces have yet to be determined, such as the kinetic rate constants in the presence of the inhibitor. In the case you mention, my recommendation would be to consider how the two types of simulations (deterministic and Monte Carlo) can complement one another to form a third, higher-level model, rather than to try to directly interlink them, which would be computationally complex, and perhaps, not the ideal approach.

**David Williams** addressed Christopher Taylor and Simon Gibbon: There is in corrosion studies a large amount of “fuzzy” data – qualitative or semi-quantitative knowledge, much of it derived from field experience or simple laboratory tests –

about what works as an inhibitor and what does not. Also, as Prof Taylor has discussed in his paper, corrosion overall is a complex process. I wonder to what extent theoretical models such as those described by Kokalj and Michaelides can be incorporated into a prediction framework along with fuzzy data, perhaps using Bayesian inference methods or techniques similar to the “land use regression” methods used in environmental science? More generally, how might the “fuzzy” data be collected and systematised so that it might be used in some such modelling?

**Christopher Taylor** replied: This is an excellent suggestion and I believe it is one that demands further inquiry. The use of data analytics methods, such as Bayesian inference, could be of value and is highly aligned with materials science initiatives currently in vogue, such as “Materials Informatics”.

**Simon Gibbon** answered: Currently insufficient use is made of modeling across corrosion studies, due to the data not have been collected at all, or not in a systematic manner. Considerable practical progress could be made by a better statistical analysis of properly collected systematic “fuzzy” data on its own. Modeling corrosion is an inherently complex challenge, as highlighted during these discussions. So there is no question that “fuzzy” data has value in modeling corrosion processes if it reduces the complexity of the modeling challenge. Bayesian inference, by allowing the incorporation of prior understanding gained from the “fuzzy” data, would provide some degree of simplification. However, the *meta*-data that goes with the “fuzzy” data also needs to be incorporated into any enhanced modeling approaches. So understanding what the “fuzzy” data relates to and the conditions under which it was acquired, may be as important to incorporate into any modeling as the “fuzzy” data itself. The applicability of modeling studies could be enhanced by using field experience to define the modeling conditions more precisely or using “fuzzy” data as a test set against which to check the trends of results.

A multi-scale modeling approach would be the best framework within which to incorporate “fuzzy” data, where inputs from quantum, molecular, fluid dynamics and other appropriate models could be used to provide a complete picture of the complex corrosion process, much as outlined in Taylor's paper. Current Bayesian modeling approaches such as those of H Wang *et al.*<sup>1</sup> looking at pipeline corrosion have not achieved the integration from the atomic scale up, but have shown excellent correlation to inspections and it is not obvious that atomic integration is necessary.

1 H. Wang, A. Yajima, R. Y. Liang and H. Castaneda, *Computer-Aided Civil and Infrastructure Engineering*, 2015, **30**, 300–316.

**Trevor Hughes** communicated: Excellent paper in terms of summarising key aspects of corrosion inhibitor design and proposing the use of a “multiphysics” modelling approach to link the various domains and microprocesses (Fig. 7 in your paper). I have two comments.

Comment 1: Perhaps the feasibility of such a modelling approach could be explored for a specific (“pilot”) system which has already been extensively studied by experimentalists and modellers. A potential candidate could be the

benzotriazole/copper system for which there is an extensive published literature and active research on modelling the inhibitor adsorption (e.g. refer to papers 10.1039/C4FD00257A and 10.1039/C4FD00273C). Another candidate might be acid corrosion inhibitors (e.g. refer to posters “*Effect of duplex steel elemental composition and microstructure on the adsorption behaviour and efficiency of acid corrosion inhibitors*”, by Man Yi Ho, Evgeny Barmatov, Jill Geddes, Lynne Crawford and Trevor Hughes”, “*Acid corrosion inhibitor film formation kinetics: experimental methods & effects of inhibitor chemistry*”, by Trevor Hughes, Evgeny Barmatov, Jill Geddes and Michaela Nagl”, and “*Effect of corrosion products on efficiency of film-forming corrosion inhibitors in hydrochloric acid*”, by Evgeny Barmatov and Trevor Hughes”) but this area is less specific in that it brings in a broad range of chemical structures, synergistic interactions and a broad range of temperature conditions.

Comment 2: Referring to the summary and conclusions section of your paper, it is stated “we acknowledge that there may be several domain-process combinations that were omitted from the model”. The fact that the corrosion inhibitor may be part of a chemical package is very important in the application of production chemicals in the oilfield. It is stated that “the intrinsic molecular stability regarding thermal decomposition or reaction with water should be given consideration” – I agree with this but I would also add that reactive (polymerisable) inhibitors are enabling in terms of the corrosion inhibitor packages used in high temperature matrix acidizing applications.

**Christopher Taylor** communicated in reply: In reference to Comment 1. I am in agreement that, having now presented a case for integrating across many different domains, some “signature problems” need to be selected collectively by a group of interested parties and the “expert teams” approach advocated in this paper applied as a demonstration of the power of the “integrated multiscale” philosophy. In reference to Comment 2. Depending on the specifics of the inhibitor problem being modeled, a set of “core physics/chemistry” modules will need to be implemented first, and then “additional” modules introduced incrementally. Deciding which physical/chemical effects are “core” and which are “additional” will have to be the prerogative of the expert team assembled to tackle the problem. I agree that, very broadly, all physical and chemical effects deemed to be significant be thrown into the mix during the initial brainstorming, and from there the team will need to downselect those effects expected to have the highest impact on the inhibitor performance. If, for example, a quantifiable expression exists for how chemicals in the package interact and modify the inhibitor effect or speciation, there seems to be no problem to incorporating it into the model.

**Gerald Frankel** opened a general discussion of the paper by Hiroki Habazaki: Does the conducting polymer still provide protection to the substrate by the mechanisms known for such polymers even though the coating is separated from the substrate by a thick oxide film?

**Hiroki Habazaki** responded: The oxide film consists of two layers; an outer porous layer with cylindrical pore structure and an inner thin barrier layer. After thermal treatment, the inner layer is transformed from amorphous to a  $\text{Fe}_3\text{O}_4$  structure, as confirmed by TEM observations.  $\text{Fe}_3\text{O}_4$  is not an insulator, showing

relatively high conductivity. In fact, the electropolymerization potential on the anodized iron after thermal treatment in argon was similar to that on passivated iron without a thick oxide layer. This suggests that the conducting polymer layer and metal substrate are electrically connected such that the conducting polymer can provide anodic protection to the substrate even if the thick oxide layer is present.

**Geraint Williams** commented: What role does cyclic re-oxidation of the reduced polypyrrole play in maintaining “ennoblement” of the iron substrate? In the presentation which accompanied the paper, an equation was displayed which represented the interaction of the oxidised form of the PPy with iron (giving Fe(II) and reduced PPy). However, this process, in isolation, would not produce the sustained high potentials (ca +0.2 V vs. Ag/AgCl) shown in Fig. 9 and 11 of your paper. Without re-oxidation of the reduced PPy, the open circuit potential (OCP) would be expected to decline with time. The fact that OCP remains time-independent upon immersion suggests one of two things. Either (i) the anodic film is stopping direct contact of the iron with the PPy and that it is simply acting as a barrier coating, or (ii) there is sufficient conductivity through the anodic film to maintain electrical contact between the iron and PPy. For the latter, the sustained OCP of +0.2V would, by implication, mean that the activity of dissolved oxygen in the electrolyte is enough to allow re-oxidation of any reduced PPy. A relatively simple experiment would allow you to differentiate between the two possibilities. If the solution is de-oxygenated (*e.g.* by sparging with nitrogen or argon) then the observation of little or no change in OCP would support option (i), while a significant decrease in OCP provides evidence in support of (ii).

**Hiroki Habazaki** replied: Thank you very much for your important comment on the role of dissolved oxygen in re-oxidation of reduced PPy. We would like to examine the immersion test under de-aerated conditions. In reduction of PPy, release of doped anions and/or incorporation of cations must occur. In fact, we found both the release of doped anions from the outer part of the PPy coating and the incorporation of sodium ions into the inner part of the PPy coating during immersion. Both processes contribute to the reduction of PPy and a decrease in the conductivity. These processes may not be reversible such that it is not clear whether re-oxidation of reduced PPy occurs and the conductivity of PPy is recovered. However, the correlation of electrochemistry and ion migration in PPy will be important for more detailed understanding of corrosion protection by conducting polymers.

**Beatriz Rico Oller** enquired: In your paper, you describe a two-step anodizing process for iron before thermal treatment in order to get a smoother substrate surface.

How different is the surface after just 1 anodizing step when compared to the one you have used? Is the adhesion of the PPy-layer that different when the iron surface has not been re-anodized? Does a second anodising not reduce the anchor effect?

**Hiroki Habazaki** responded: The first step anodizing and its film dissolution were used just as a replacement of mechanical polishing using alumina paste.

Then, we were able to get reproducible results. Without any surface pretreatment, the surface appearance of the anodized specimens was not uniform; Pores with non-uniform pore sizes were obtained. After two-step anodizing, pores of ~30 nm diameter were developed uniformly on the entire surface, providing sufficient anchor effect to the PPy layer.

**David Williams** asked: Could this coating advantageously be used as a primer for painting, so that corrosion inhibitor could be released below the paint coat?

**Hiroki Habazaki** answered: Although we have not yet studied our composite coating as a primer for painting, there have been several studies demonstrating a beneficial role of a conducting polymer layer as a primer to improve the corrosion protection. Some references are as follows: ref. 1–3.

1 K. Kamaraj, V. Karpakam, S. S. Azim and S. Sathiyarayanan, *Synth. Met.*, 2012, **162**, 536.

2 T. Y. Pan and Z. Y. Wang, *Microsc. Res. Tech.*, 2013, **76**, 1186.

3 S. U. Rahman, M. A. Abul-Hamayel and B. J. A. Aleem, *Surf. Coat. Technol.*, 2006, **200**, 2948.

**Stuart Lyon** remarked: Does the corrosion resistance depend on the oxide thickness in any way?

**Hiroki Habazaki** responded: The thickness of the porous layer did not influence the corrosion protection a lot, with a thickness of up to 2 micrometers, while the thickness of the conducting polymer layer changed the durability of the coating a lot.

**Julian Wharton** enquired: The anodization electrolyte contains a small amount of water ( $0.5 \text{ mol L}^{-1} \text{ H}_2\text{O}$ ), as such there is likely to be some residual water at the metal/anodic film interface. Please comment on the influence of this residual water on the fluoride diffusion and also how it may affect the thermal oxide growth during heat treatment in both argon and air.

**Hiroki Habazaki** answered: The water concentration in anodizing electrolytes influences significantly the growth of porous anodic films on iron. At relatively high water concentrations, gas generation is enhanced and the efficiency for film growth is reduced. At high water concentrations, crystalline oxide nanocrystals, which may act as sites for gas generation, are more readily formed in the barrier layer of the anodic films on iron.<sup>1</sup> In the barrier layer, a high electric field is applied such that water content is negligible at the metal/anodic film interface. In addition, fluoride migrates inwards faster than oxide ions, resulting in the formation of  $\text{FeF}_3$  just above the metal/anodic film interface, regardless of water concentration. For thermal oxide growth, no large influence of water concentration may be expected, although we have not yet conducted the detailed study.

1 H. Habazaki, Y. Konno, Y. Aoki, P. Skeldon and G. E. Thompson, *J. Phys. Chem. C*, 2010, **114**, 18853.

**Angus Cook** commented: In Fig. 4(a) of your paper, the GDOES depth profile of fluorine (F) seems to have a very regular intensity variation before reaching the M/F interface. The same variation is not seen in any of the other surveyed species.

Could you comment on the reason for this intensity variation within the applied film?

**Hiroki Habazaki** replied: Wavy profiles in GDOES are obtained sometimes when transparent films on metallic substrates are analyzed. The wavy profile is an artefact, originating from interference of light emitted from fluorine in the anodic film. So, this intensity variation does not reflect the compositional variation.

**Ann Wilson** communicated: My question follows on from Prof Williams' question. I have attempted some adhesion studies for PPy at mild steel and found that while the deposition of an oxide layer on the metal surface resulting from flaming of the metal electrode improves adhesion of PPy, often there appears to be no contact between the metal surface and the electroactive polymer film, leaving me to think that PPy acts only as a barrier film and does not allow for electro-protection of the metal. What is your experience as far as this is concerned with the PPy films over the anodized layer?

**Hiroki Habazaki** communicated in reply: We believe the electric contact between the PPy and metal substrate from the following findings.

1. The oxide located between the PPy in pores and iron substrate is  $\text{Fe}_3\text{O}_4$ , which is well-known to show high electric conductivity, not an insulator.
2. The potential of electropolymerization on the anodized iron after thermal treatment in argon is similar to that on the passivated iron, although the electropolymerization occurred at higher potential on the anodized iron after thermal treatment in air.
3. For the anodized iron after thermal treatment in argon, the electropolymerization occurs on the entire pore wall surface, not only at the pore bottom. This means that pore walls, mainly consisting of  $\text{Fe}_3\text{O}_4$ , have sufficiently high electric conductivity for electropolymerization of PPy. From these findings, at least for the anodized iron after thermal treatment in argon, the PPy layer should be electrically connected sufficiently to the metal substrate, and anodic protection must be contributing the corrosion protection, in addition to the barrier nature of PPy.

**Simon Gibbon** opened a general discussion of the paper by Line Kyhl: Please could you explain how graphene on diamond is able to trap super critical steam on the diamond surface such that the steam destroys the diamond leaving the graphene intact,<sup>1</sup> but in your work graphene was not able to protect platinum from salt water at 60 °C? Would edge functionalisation of the graphene give better resistance to salt water?

1 C. H. Lim, A. Sorkin, Q. Bao, A. Li, K. Zhang, M. Nesladek and K. P. Loh, *Nat. Commun.*, 2013, **4**, 1556.

**Line Kyhl** replied: In their work on graphene–diamond systems, Lim *et al.* concluded that after heating to 1275 K, carbon atoms at the graphene–diamond interface could form strong covalent bonds. As the graphene sheet lay buckled on the diamond surface, the formation of these covalent bonds led to the evolution

of nanobubbles, somewhat like buckyballs, with an sp<sup>2</sup> hybridised cage (graphene layer), with the lower part of the ball consisting of weaker sp<sup>3</sup> hybridised bonds; the diamond surface. Water molecules were trapped inside these cages. After heating the system above the super critical limit of water, Lim *et al.* reported an etching of the diamond and not of the graphene. This indeed proves that the sp<sup>2</sup> carbon allotropes are extremely inert and impermeable. It was the strong interfacial bonds that were key in this experiment. These interfacial bonds effectively sealed the edges of the graphene and inhibited the trapped water from diffusing out of the nanobubbles, creating a pressure cooker, with super-heated water molecules trapped inside. These super-heated water molecules then began to etch the diamond surface. Thus, the graphene-diamond system prepared by Lim *et al.* offered a unique possibility to study the behavior of small confined areas of defect-free, edge-sealed graphene.

Taking our experiments with graphene on Pt(100) into perspective, the graphene edges here form carbon–metal bonds. These bonds will be weaker than the strong carbon–carbon interfacial bonds formed by graphene and diamond. The weaker C–metal bonds may more easily be compromised, allowing corrosion-inducing reactants to intercalate and gain access to the Pt surface.

Regarding the second part of your question: if the mechanism for coating breakdown depends on the ability of intercalants to diffuse beneath a graphene domain edge or defect site, then one would expect that an increased interaction between the graphene edge and the substrate would prevent intercalation. This effect may be provided by functionalization and would thus offer an increased corrosion protection. Functionalizing the graphene basal plane may lead to a stronger interaction with the substrate. This effect is seen, for example, with hydrogen functionalized graphene on Ir(111),<sup>1</sup> and is thus expected to hinder the diffusion of intercalated species.

1 R. Balog, M. Andersen, B. Jørgensen, Z. Sljivancanin, B. Hammer, A. Baraldi, R. Larciprete, P. Hofmann, L. Hornekær and S. Lizzit, *ACS Nano*, 2013, 7, 3823–3832.

**Hendrik Bluhm** asked: The stability of the graphene layer on Pt(100) against intercalation by gas phase molecules is surprising, given that, *e.g.*, oxygen and CO intercalation has been observed already at millibar or lower pressures for graphene layers grown on other metal single crystal surfaces. What explains the increased stability of the graphene layer on Pt(100) against intercalation?

**Line Kyhl** answered: CO has been reported to intercalate both graphene on Pt(111)<sup>1</sup> and Pt(100)<sup>2</sup> at partial pressures of 10<sup>−6</sup> mbar and above. In the case of graphene on Ir(111) where the interaction between the graphene layer and the metal surface is relatively strong, a CO pressure in the mbar regime is necessary to force intercalation.<sup>3</sup> In this latter case, the adsorption pattern which CO forms on Ir(111) below the graphene was found to be identical to the adsorption pattern of CO adsorbed on bare Ir(111), when exposed to the same partial pressure of CO in the mbar regime. This shows that a certain coverage of CO on the substrate is needed to make intercalation favorable. Oxygen has been shown to intercalate graphene on Pt(111), but only through channels of delaminated graphene, which were fabricated by first intercalating CO. On graphene on Ir(111) elevated sample temperatures are needed for oxygen intercalation to happen.<sup>4</sup> There is no



evidence from our results that graphene on Pt(100) has increased nor decreased stability towards oxygen intercalation, when compared to the above findings for graphene on Pt(111) or graphene on Ir(111). The stability towards CO intercalation, however, is lower for this system (Pt(100)) than for graphene on Ir(111) in the sense that a lower partial pressure of CO is needed for intercalation to proceed.<sup>2</sup> It is peculiar that CO intercalates graphene on metal surfaces, at room temperature, at a partial pressure which is substrate dependent. The mechanism for oxygen intercalation must be different to that for CO intercalation, since the same dependence on partial pressure is not observed, and instead the substrate temperature appears to be the relevant parameter.

- 1 R. Mu, Q. Fu, L. Jin, L. Yu, G. Fang, D. Tan and X. Bao, *Angew. Chem.*, 2012, **124**, 4940–4943.
- 2 L. Nilsson, M. Andersen, R. Balog, E. Lægsgaard, P. Hofmann, F. Besenbacher, B. Hammer, I. Stensgaard and L. Hornekær, *ACS Nano*, 2012, **6**, 10258–10266.
- 3 E. Grånäs, M. Andersen, M. A. Arman, T. Gerber, B. Hammer, J. Schnadt, J. N. Andersen, T. Michely and J. Knudsen, *J. Phys. Chem. C*, 2013, **117**, 16438–16447.
- 4 E. Grånäs, J. Knudsen, U. A. Schröder, T. Gerber, C. Busse, M. A. Arman, K. Schulte, J. N. Andersen and T. Michely, *ACS Nano*, 2012, **6**, 9951–9963.

**Stephen Lyth** commented: Recently it has been shown that graphene and graphene oxide are permeable to protons.<sup>1–3</sup>

Could ion transport through the graphene coating be responsible for corrosion in NaCl solution at elevated temperature? Repeating the corrosion studies especially in acidic conditions may shed light on this possible mechanism.

- 1 J. L. Achtyl, R. R. Unocic, L. Xu, Y. Cai, M. Raju, W. Zhang, R. L. Sacci, I. V. Vlasiouk, P. F. Fulvio, P. Ganesh, D. J. Wesolowski, S. Dai, A. C. T. van Duin, M. Neurock and F. M. Geiger, *Nat. Commun.*, 2015, **6**, 6539.
- 2 S. Hu, M. Lozada-Hidalgo, F. C. Wang, A. Mishchenko, F. Schedin, R. R. Nair, E. W. Hill, D. W. Boukhvalov, M. I. Katsnelson, R. A. W. Dryfe, I. V. Grigorieva, H. A. Wu and A. K. Geim, *Nature*, 2014, **516**, 227–230.
- 3 T. Bayer, S. R. Bishop, M. Nishihara, K. Sasaki and S. M. Lyth, *J. Power Sources*, 2014, **272**, 239–247.

**Line Kyhl** responded: It has been calculated that an open configuration of the graphene edge is favorable in the presence of OH<sup>−</sup> groups.<sup>1</sup> For a basic solution with a surplus of OH<sup>−</sup> ions, the above open edge configuration may occur, allowing sodium and chloride ions and water to intercalate. Other mechanisms, such as the direct diffusion of OH<sup>−</sup> or H<sup>+</sup> ions through the graphene basal plane may be a possibility. A full study using solutions of varying pH would be interesting, as you suggest. If the scenario involving OH<sup>−</sup> groups binding to the graphene edges is correct, one should observe a higher degree of protection against the acidic solutions.

- 1 L. Nilsson, M. Andersen, B. Hammer, I. Stensgaard and L. Hornekær, *J. Phys. Chem. Lett.*, 2013, **4**, 3770–3774.

**Vincent Maurice** commented: I find the work quite interesting but wonder if the same conclusions on the protectiveness of the graphene layer would apply to a different substrate. In the present case of the platinum surface, stability of the graphene layer and corrosion protection is concluded as long as surface reconstruction is not lifted, which is a 2D surface transformation. Would the graphene

layer be as protective on a substrate, where exposure to oxygen or water leads to a 3D growth of an oxide layer?

**Line Kyhl** commented in reply: When oxygen or water penetrate a graphene layer to react with the underlying substrate this occurs through defects or the edges of graphene domains. In the case of graphene on Pt(100) the effectiveness of the coating was in our work probed by detecting the lifting of the surface reconstruction below the graphene. Observation of a lifted surface reconstruction was taken as evidence that reactants had penetrated the graphene sheet to react with the underlying Pt surface, a 2D transformation. Our experiment was thus designed to study the effectiveness of graphene as an impenetrable barrier. Hence, on this basis, there will be no difference in the graphene barrier properties between a substrate with the possibility for 3D corrosion processes and the Pt(100) model substrate. With the proviso that 3D corrosion, as it is not necessarily a surface process, may not be as readily detectable as the 2D transformation which leads to the lifting of the Pt surface reconstruction.

On the other hand there is no doubt that a graphene layer will bond differently to different substrates depending on the adhesion between the substrate and the graphene layer. On Pt(100) the graphene-edge C-atoms bind down to nearby Pt-atoms, thereby closing for the immediate penetration of water or oxygen.<sup>1</sup> This favorable, closing-off effect, where graphene edges are sealed with the underlying substrate, may vary between different metal surfaces. Furthermore, any evolution of an oxide layer below the graphene may lead to a delamination of the graphene coating.

1 L. Nilsson, M. Andersen, B. Hammer, I. Stensgaard and L. Hornekær, *J. Phys. Chem. Lett.*, 2013, **4**, 3770–3774.

**Rob Lindsay** remarked: In your paper, you mention that transferring a graphene layer to another substrate introduces numerous defects. Could you please expand on this comment, indicating the type of defects introduced. This issue also suggests that engineering application of a graphene coating for corrosion control (*e.g.* for protection of an oil pipeline) may be impractical, as the environment will inevitably be much harsher. What is your opinion?

**Line Kyhl** replied: If domain boundaries are present from the graphene growth as, *e.g.*, is the case of graphene on Cu films, the sheet is susceptible to rupture along these domain boundaries during transfer processes. This gives rise to a transferred film consisting of flakes rather than one continuous sheet. Point defects on the graphene basal plane may be introduced during transfer methods involving electrochemical reactions. This may compromise the corrosion protection as the diffusion barrier for corrosive molecules or atoms may be lower at these defect sites. As an example, the diffusion barrier for oxygen at such a site has been calculated to become significantly lowered relative to oxygen diffusing through an intact hexagonal ring of the graphene basal plane.<sup>1</sup> Often the transfer methods additionally include using a polymer resist, which can be difficult to remove from the transferred graphene. Whether or not these polymer residues have an influence on corrosion protection is unclear.

Generally, graphene grown on substrates with a stronger interaction between the graphene and metal gives more uniformly oriented nucleation sites and better epitaxial growth. This leads to better quality of the graphene. This high degree of interaction gives rise to high adhesion between the graphene sheet and the substrate, which poses challenges for any transfer process. Therefore a high quality graphene usually demands a transfer scheme involving harsher electrochemical conditions in order to detach it from its substrate.

On the other hand, transferring high quality graphene sheets from graphite, where there is poor adhesion between the sheets, can be done gently without introducing defects. However, only small flakes can be produced in this way. Transferring several layers of graphene on top of each other to a metal surface has been shown to decrease the corrosion rate when compared to a single transferred layer.<sup>2</sup> The authors concluded that defects from the transferred layers are unlikely to be in registry and the metal surface therefore essentially becomes entirely covered by intact graphene. The lowest corrosion rate found in the study, however, was that of a metal with a graphene coating directly grown on the surface. Non-destructive transfer methods are continuously being developed. This may enable the future application of using transferred graphene as a protective coating material. However, the direct growth of a graphene coating on the metal surface may show to be more advantageous.

1 M. Topsakal, H. Şahin and S. Ciraci, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2012, **85**, 155445.

2 D. Prasai, J. C. Tuberquia, R. R. Harl, G. K. Jennings and K. I. Bolotin, *ACS Nano*, 2012, **6**, 1102–1108.

**Tom Majchrowski** requested: This is an interesting application of Raman spectroscopy for corrosion studies. In the presented Raman spectra there is a significant shift (approx  $50\text{ cm}^{-1}$ ) in the position of the D, G and 2D signals after exposure to saltwater at  $60\text{ }^\circ\text{C}$ . In the paper you explain the shift in the position of the signal by considering hybridization or change in the graphene strain. I think there is significant change taking place in the chemical environment around that vibrating bond. Would you be able to present your thoughts on this in more detail?

**Line Kyhl** answered: A sample temperature of  $800\text{ }^\circ\text{C}$  was reached during the preparation of the graphene coating. The thermal expansion coefficient of the metal is much larger than that of the graphene. Because of this, the graphene will experience a compressive stress when the sample is cooled. This compressive stress shifts the vibrational energies of the raman active phonons towards higher wavenumbers, when compared to freestanding, relaxed graphene. Furthermore a hybridization of the graphene pz orbitals and Pt d orbitals leads to a distortion of the carbon lattice, again increasing the vibrational energy of the phonons. Moreover, the intensity of the Raman signal is screened by the metal surface leading to a significant decrease in intensity compared to what is observed for graphene on insulating substrates. Upon exposure to hot saltwater the D, G and 2D graphene peaks shift towards lower wavenumbers and increase in intensity. The peaks thus change to resemble those of a more freestanding graphene, less influenced by the metal surface below. Under the saltwater exposure the Pt surface reconstruction becomes lifted, but there is no evidence that the graphene

lattice is chemically modified from this exposure. We therefore conclude that the graphene relaxes and becomes quasi-freestanding.

**Christopher Taylor** asked: As a surface becomes progressively more rough, is there a limit at which point graphene can not be smoothly applied to the surface? As a separate question, what developments have been made in the application of graphene oxide, reduced graphene oxide, and functionalized graphene/graphene-oxide surfaces to corrosion protection of metals?

**Line Kyhl** responded: It is possible to bend and stretch the graphene lattice ~20% away from its equilibrium, free-standing, state.<sup>1</sup> Studies of graphene growth on rough surfaces are scarce. The usual growth mechanisms may be inhibited by a rough surface, but a transferred graphene film should essentially be unaffected by a surface roughness on the  $\mu\text{m}$ -scale. A defect-free single crystalline, single layer graphene sheet as an anti-corrosion coating is unlikely to be obtainable. One possible method to increase the protective properties of a defected coating is to apply several layers on top of each other, to cover defects. A cheap and easy method for obtaining multilayers of graphene-based sheets on a substrate is by applying graphene oxide (GO) or reduced graphene oxide (rGO). GO is impermeable to most atoms and molecules, even helium, but under humid conditions water can readily penetrate.<sup>2</sup> Reducing the GO, however, using hydroiodic acid has been shown to lead to leak-tight coatings.<sup>3</sup> The water can penetrate the GO multilayers through capillaries formed in the interlayer spacing with a width of ~10 Å.<sup>2</sup> After reduction, the interlayer spacing approaches that of graphite and none of the tested gases, liquids, salt or acids could penetrate. The reduction method is key to obtain a high quality rGO anti-corrosion coating. Thermally reduced GO films contain numerous structural defects, which compromise the mechanical strength of the sheet. Furthermore, a high density of non-reduced moieties allows for the penetration of water. To summarize, the work of Su *et al.* indicates a possible route for creating an almost defect free corrosion protective coating, superior in quality to CVD graphene, using GO as a starting point.

1 C.-L. Wong, M. Annamalai, Z.-Q. Wang and M. Palaniapan, *J. Micromech. Microeng.*, 2010, **20**, 115029.

2 R. R. Nair, H. A. Wu, P. N. Jayaram, I. V. Grigorieva and A. K. Geim, *Science*, 2012, **335**, 442–444.

3 Y. Su, V. G. Kravets, S. L. Wong, J. Waters, A. K. Geim and R. R. Nair, *Nature Commun.*, 2014, **5**, 4843.

**Sonja Nixon** enquired: Can you speculate about future industrial feasible applications of graphene? Are there any limitations for industrial applications to be expected especially when we consider the PVD high temperature deposition process?

**Line Kyhl** replied: A discussion of the outlook for future applications is not trivial. For each application one must consider the quality or type of graphene needed. This leads to the question of what graphene is, which in the literature has a wide span. For example multilayer sp<sup>2</sup> carbon flakes or heavily functionalized sheets are often referred to as graphene in the same contexts as a single layer, single crystalline sp<sup>2</sup> carbon sheet with low defect density. Each grade or type of

graphene might be useful for different application scenarios and is accompanied by its own set of qualities, limitations and challenges. High growth temperatures in the CVD and PVD processes are usually undesirable for industrial applications. For applications in anti-corrosion coatings, phase changes, during the heating processes, in the material on hand may compromise the desired mechanical properties. Another challenge is applying the carbon precursors to the hot material in a controlled manner. Nonetheless research into alternative low temperature growth methods is a hot topic.<sup>1</sup>

1 T. Wu, G. Ding, H. Shen, H. Wang, L. Sun, Y. Zhu, D. Jiang and X. Xie, *Nanoscale*, 2013, 5, 5456–5461.

**Sonja Nixon** opened a general discussion of the paper by Peter Visser: We can control very precisely the pH during chemical conversion coating processes. During the corrosion process the pH depends on many factors. How sensitive is the corrosion protection mechanism by the lithium salts and how can it be controlled? Does the coating or the interface to substrate degrade during the leaching and the corrosion process? In the figure of your paper, the coating beside the scribe looks opaque after exposure to the salt spray.

**Peter Visser** answered: As demonstrated from the literature cited in the paper, the protective layer will be formed at alkaline pH. In contrast to the chemical conversion process, the pH must be controlled with the leachable species from the coating. In this study the uninhibited coating does not contain pigments and is transparent. The lithium-salt loaded coatings contain a pigmentation package and therefore they are opaque.

**Julian Wharton** asked: Have the authors quantified the lithium-ion leach rates from the polymeric coatings? In addition, please give the rationale for using a 100  $\mu\text{m}$  deep scribe in the AA2024-T3 substrate, as opposed to just coating removal down to the metal surface. Were the panels in a standard orientation within the neutral salt spray testing and if so were there any morphological differences in inhibition performance between the top and bottom of the panels?

**Peter Visser** replied: For both model systems the leach rate from the polymeric coatings has been determined. Due to the difference in solubility of lithium oxalate and carbonate a large effect has been observed on the leach rate. The concentrations of the lithium oxalate coatings are about 10 to 20 times higher compared to the lithium carbonate. However, both species provide similar protective layers. The rationale for the 100  $\mu\text{m}$  deep scribe originates from the specification requirements of the aerospace industry. The panels were exposed according to the ASTM-B117 requirements at a 6° angle. No performance difference between the top and bottom of the panels was observed.

**Gerald Frankel** questioned: Have you studied the throwing power? How far from a cut edge can be protected? Have you calculated or modeled the transport of the Li ions across the surface? The protection must be a function of time and distance? What concentration is needed for protection?

**Peter Visser** answered: This particular study represents the first observations of the protective film when using lithium leaching salts in an organic coating. The throwing power of this system has not been studied yet. Indeed, the inhibitor efficiency is an important parameter when considering their potential use. The throwing power will be an important factor in this inhibitor efficiency, which is influenced by the amount of inhibitor, the type and thickness of the coating. Another factor would be the presence of a topcoat influencing the water flux and inhibitor diffusion from the coating. No modeling or further calculations were performed so far. In prior art the protective layers were generated from high pH (>11) and saturated aluminate solutions. These results demonstrate the activity of the lithium ion at much lower concentrations and pH values. Hence such throwing power, modeling and detailed calculations will be focus points of a research study in the near future.

**Rob Lindsay** asked: Have you attempted to study what happens if you re-scratch an inhibited scribed area, *i.e.* is this area also inhibited?

**Peter Visser** responded: No, this was not done for this system. However, some unpublished work revealed inhibition of a new scribe right next to (*i.e.* 2 mm from) a protected scribe after saltspray exposure was resumed.

**John Scully** commented: Given the Li treatment described and the coverage of the bare Al alloy scratch shown, do you think that the treatment enables cathodic inhibition, anodic inhibition or both? A series of electrochemical experiments on both the alloys and separately on the constituent particles present in the alloy might help address this question. It seems that the thick film shown could provide a means of cathodic inhibition of transport of oxygen to the Al-Cu-Fe, Al-Cu, or Al-Cu-Fe-Mn co-constituent particles, which otherwise may see fast O<sub>2</sub> transport in thin electrolyte films. Have you considered adding another chemical species to provide a second inhibitor function?

**Peter Visser** replied: Prior literature on the lithium based conversion coatings and some unpublished electrochemical work indicate that the inhibition due to the lithium based inhibitor leaching does not exhibit clear anodic or cathodic inhibition behavior as some well-known inhibitors (*e.g.* benzotriazole) of aluminium alloys. The thick protective film is essentially formed by the grace of the alkaline corrosion reaction and follows upon the formation of the aluminium hydroxide layer and is exclusively due to the presence of the lithium ion. Indeed, the oxygen reduction reaction has been inhibited due the layer formed on the entire surface of the alloy, including the intermetallic particles. Possible damage to and local defects in the protective layer can potentially lead to further local corrosion.

Finally, yes we are investigating the addition of additional species to the coating formulation to even further enhance the corrosion inhibition.

**Geraint Williams** remarked: Most lithium salts are highly water soluble, so I'm slightly surprised that lithium carbonate and oxalate salts can be used as sparingly soluble pigments in a primer coating. Is there a danger of the lithium salts deliquescing and causing osmotic blistering of the protective coating during long-

term immersion? Has the use of ion-exchange based minerals, so-called “intelligent release” pigments, such as bentonites and zeolites, been considered as a possible alternative method of storing and releasing the Li(i) cations? Finally, although salt-spray testing is a useful benchmark for the comparison of the protective ability of various coatings, a more realistic evaluation of the corrosion resistance of coatings for AA2024 aerospace alloy is typically achieved using a Lockheed test, where coating failure *via* filiform corrosion (anodic disbondment) predominates. Is there any evidence to suggest that in-coating lithium cations would inhibit this type of underfilm corrosion?

**Peter Visser** answered: Lithium carbonate and lithium oxalate are the two least soluble pigments next to lithium phosphate. Indeed, coating formulation must be carefully balanced to prevent the effect of osmotic blistering. This particular study focused on the primary effects of the use of lithium salts in coatings. Alternative delivery methods of Li cations are being considered for further research. Both saltspray and filiform corrosion tests are widely used and required to assess the corrosion resistance of coatings for AA 2024-T3. Both types of corrosion have different mechanisms. In this study filiform corrosion has not been evaluated, but shall be in the near future.

**Trevor Hughes** communicated: This is an interesting study leading to a proposed mechanism for the formation of a protective layer (Fig. 12 of your paper). My comment is based on my experience of studying aluminium hydroxide gels in the context of their use as delayed gels for blocking excessive water production in oilfield reservoirs. The successive addition of OH<sup>-</sup> ions to an acidic aqueous solution of Al chloride leads to the formation of an aluminium hydroxide gel whose strength mainly depends on the total concentration of Al in the system. The pH at which such gels begin to form is around 5.5. In terms of understanding the composition and properties of the gel, the onset of gelation is more conveniently defined in terms of an OH/Al ratio of the system. Beyond the OH/Al ratio required for the onset of gelation, with further addition of OH<sup>-</sup>, the average OH/Al ratio of the system increases further towards a value of 3 (corresponding to the thermodynamically stable phase gibbsite Al(OH)<sub>3</sub>) and beyond to the non-gel regime dominated by Al(OH)<sub>4</sub><sup>-</sup>(aq). The kinetic stability of aluminium hydroxide gels depends on the OH/Al ratio of the system – those with OH/Al ratio < 3 are more stable than those at OH/Al = 3. There is a large body of literature on the characterisation of such gels in terms of constituent poly-nuclear Al species and inorganic polymers formed from the tridecamer, Al<sub>13</sub>O<sub>4</sub>(OH)<sub>24</sub>(H<sub>2</sub>O)<sub>12</sub><sup>7+</sup> (commonly known as the “Al<sub>13</sub>” cation). In the context of the present paper, it would be interesting to characterise Li-doped aluminium hydroxide gels in terms of their pH limits and their kinetic stability – as mentioned in the paper, the nature and properties of the associated anion (carbonate, oxalate,...) will also have important effects on the properties and stability of the gel.

**Peter Visser** communicated in reply: Thank you very much for this comment and suggestions. This literature can be of great value. The interaction of lithium with the aluminium hydroxide gel seems to be very important to obtain the inhibitive effect observed. However, the detailed role or function of lithium in the stabilization of the aluminium hydroxide gel is not well understood as yet. The

characterization of these Li-doped aluminium hydroxide gels could provide more insight.

**Julian Wharton** opened the discussion of the paper by Suzanne Morsch: High-purity water can rapidly pick-up contaminants such as carbon dioxide that can affect its pH. Was the pH or resistivity assessed during the pre-exposures in deionised water to establish that the water maintained its high quality over the 7 day immersion?

**Suzanne Morsch** responded: The pH was not assessed during a 7 day immersion. However, epoxy-phenolic resins are renowned for chemical resistivity, so that slight changes in pH are not expected to degrade the coating directly. Contamination of the water may however be expected to affect water sorption as a consequence of reduced water activity. We recently examined coatings exposed to 5% (w/w) aqueous NaCl solutions and found that morphological changes were attenuated under these conditions.

**Sonja Nixon** questioned: Does the investigated coating contain any pigments? Can the method for determination of water uptake be applied for pigmented coatings?

**Suzanne Morsch** replied: The investigated coating did not contain pigments, it is a simplified epoxy-phenolic lacquer (thermoset polymer). The *in situ* FTIR experiment described could be applied to measure water sorption for a pigmented coating, provided that sufficient transmission is possible to acquire a reflection mode spectrum. We have found this to be highly dependent on the coating thickness. In the case of AFM-IR, we have previously analysed pigmented primers and are able to acquire localised spectra and images with relative ease. One possible complication arises for such coatings, where the effective sampling depth varies locally as a result of the underlying pigment particles. This can be circumvented by mapping an IR-induced amplitude at several wavelengths (corresponding to peaks in the IR spectrum), and then generating a ratio image (since any variation in the signal due to the film thickness should cancel out).

**Julian Wharton** asked: How long did it take to perform a typical AFM-IR area scan and also what were the criteria for assessing AFM cantilever tip contamination?

**Suzanne Morsch** answered: The AFM-IR images acquired for this work were scanned within approximately 2 h. In this particular case 32 co-averages were taken for the photothermally induced ring-down at each point, in order to enhance sensitivity towards small changes in IR absorbance accompanying water uptake, and this requires an unusually slow scanning speed. Typically, AFM-IR scans may be performed in as little as 20 min. However, this does not include the time required for the system set-up, *i.e.*, to perform laser alignment and IR background scans. Since AFM-IR imaging is necessarily performed in contact mode, tip contamination can be an issue. Generally speaking, tip contamination is apparent from streaking or blurring effects in height scans, particularly over



small scan areas, as in conventional AFM imaging. If a contaminant is IR active, contamination may also be apparent from IR spectra obtained using the probe.

**David Shoemith** remarked: You demonstrate clearly that the coating develops bubbles due to the accumulation of water in void locations within the coating. Does this introduce a physical stress in the coating, and, if so, what are the consequences for the stability of the coating? Having developed such voids, can you explain how they lead subsequently to ionic pathways through the coating? Is it possible to deposit a coating without any void space?

**Suzanne Morsch** responded: In polymers, a proportion of the free volume is known to exist as nanovoids associated with chain ends, the size and distribution of which is such that some are capable of housing water molecules. For conventional organic coatings, such as epoxy networks, such voids are known to be present, and appear to be an inherent feature of amorphous polymer networks. Since we propose that nanovoids are enlarged by spontaneous polymeric relaxation in the presence of water, this process is considered to be a consequence of increased overall thermodynamic stability. It is expected that during prolonged immersion swelling stresses generated in the coating would eventually restrict any further growth of such voids, so that an equilibrium morphology/water content is eventually reached. Indeed recent examination of epoxy-phenolic samples immersed in deionised water for 3 weeks, and also after immersion for 10 months, revealed comparable morphologies to those we reported here for samples soaked for 1 week. We have not directly measured stress, although coating delamination is never observed. Long term degradation of the corrosion protection provided by intact organic coatings has previously been proposed to occur *via* hydrophilic channels which eventually widen to form ionic pathways. This work represents some of the first direct evidence cases for the long-term formation of such hydrophilic pathways, since voids contain clustered, bulk-like water. It can be envisioned that since polymers are dynamic systems, established void regions may migrate/deform during prolonged immersion, so that ionic transport through the coating becomes possible, although we have no direct evidence for this at present.

**Simon Gibbon** commented: People don't normally think about the water that polymers contain. In reality all polymers absorb an equilibrium quantity of water dependent on their specific chemistry and the environment. However, coatings protect against corrosion despite containing water. This work is aimed at understanding what changes cause corrosion to occur after a long period of time.

**Ying-Hsuan Chen** asked: Have you tried immerse the sample again in DI water after drying the sample? A second cycle of drying?

**Suzanne Morsch** answered: We have not done this experiment. Several aging studies have however reported that cycled immersion and drying yields faster water sorption kinetics together with a greater volume of sorbed water for epoxy resins. This is presumably because polymeric relaxation in the presence of water is frozen into place on drying. We suspect that after prolonged immersion or numerous cycles an equilibrium conformation would be reached whereupon no

further increases in kinetics/water content would be detected, however this is a subject of on-going research.

**Stuart Lyon** remarked: The challenge for this and related work is to consider and validate (or exclude) hypotheses relating to the performance of coatings – some of these derive from the 1960s and, while intellectually compelling, have never been experimentally verified. Working below the diffraction limit allows, for the first time, spectroscopic identification of functional group chemistry (*i.e.* arising either from intrinsic differences in the polymer or from the segregation of small molecular mass species, such as water) in polymers at a length scale of 50–100 nm.

**Christopher Taylor** opened the discussion of the Concluding remarks by John Scully: A new cost of corrosion study is underway, in partnership between DNV GL and APQC. The new study will extend beyond previous studies – limited to the US – to consider the global impact of corrosion, and strategies to mitigate these impacts and costs (see the NACE press release at the URL shown in ref. 1).

1 <http://www.nace.org/Newsroom/Press-Releases/NACE-International-Institute-Selects-DNV-GL-and-APQC-as-Research-Partners-on-Global-IMPACT-Study/>

**Alison Davenport** responded: Studies of this type are vital to make the case to the government for further investment in research and developing skilled people. It is particularly valuable that this study considers the global impact of corrosion. It would be very helpful if such studies were also conducted in the UK and other countries to highlight the economic and societal impact of corrosion.