Faraday Discussions

Cite this: *Faraday Discuss.*, 2015, **180**, 381

Localised corrosion: general discussion†

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DOI: 10.1039/c5fd90046h

Philippe Marcus opened a general discussion of the paper by Roger Newman: Should the passive film not be significantly involved in pit initiation (as you suggest), how would you explain that the time to initiation is very much dependent on the nature of the passive film?

Roger Newman responded: I never said that the passive film is not involved in pit initiation. I understand (of course) that longer passivation gives a longer induction time for pitting. What I say is that the effects of parameters like alloy composition, environment composition, potential, and temperature, are not easily accommodated (at least not predictively) within a passive film breakdown model, but fall out naturally from a modified Galvele type of model that uses pitting potential data (or, if one has the time, lower extremes of pitting potential distributions). Now I don't know whether or not the finest details of film breakdown, detectable at the pA level or lower in electrochemical experiments (not nA to μA – those are already pits), and/or on very pure, flat alloy surfaces, follow the same rules that we find using pitting potentials on industrial or semi-industrial alloys. Those measurements have not been done. Actually I don't think stainless steel is necessarily the best model system for such studies. Under certain conditions, as shown by Bardwell many years ago, iron shows blizzards of pits that are clearly not impurity-particle-related; probably aluminum too. In stainless steel we really don't know whether pit initiation ever occurs without a microcrevice and/or an impurity particle.

From the viewpoint of practical utility, the Galvele type of approach clearly has the advantage. The Critical Pitting Temperature (CPT) is a propagation-related transition below which metastable pits never become stable at any potential. My group has published extensively on that. One can make a foolproof, if expensive,

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† Electronic supplementary information (ESI) available: SVET scans movie. See DOI: 10.1039/c5fd90046h

alloy selection by looking up CPT values for different alloys. Their resistance to passive film breakdown is wholly irrelevant so far as temperature effects are concerned.

John Scully asked: Your paper discusses several important dissolution nuances such as the way Fe and Ni dissolve during corrosion and how that is affected by sulfur. Has our understanding advanced regarding how a nickel or iron atom oxidizes given different first and second nearest neighbor arrangements such as in multi-element solid solutions?

Roger Newman replied: We are dealing here with what Pickering would have called region 3 dealloying – that is, Ni enriches during simultaneous dissolution, without (as far as we know) porosity formation. Some insights have been gained on Pickering's region 1 dealloying (low potential, only one element dissolving – not really accessible for FeNi) through work of Sieradzki and (for an initially ordered alloy) Renner. Also, Erlebacher's MESOSIM simulation can change the "bond energies" and examine the resulting kinetics and morphology.[1–4] But simultaneous dissolution is harder to study. Clearly Ni dissolution limits, in a way, the dissolution of the whole alloy, and if the Ni dissolution is activated by S adsorption, then the alloy will dissolve faster (of course Fe dissolution is also activated). Regarding the effect of Ni content on this surface enrichment and its consequences, I don't believe a systematic study has been done for the FeNi system, and surface analysis of dissolved or dissolving samples is a huge challenge. Obviously one doesn't get exactly the same polarization curve for 5% Ni as for 50% Ni, and when I tried this (on a small scale) I remember having problems with martensite at certain Ni content. Experimentally, it would be nice if there was a binary alloy of more noble metals that could be subjected to either simultaneous or selective dissolution depending on the potential, with no interference from hydrogen evolution, but the usual Au alloys in simple acids are not suitable for that, and many other systems have bad phase diagrams. Possibly one could use a complexing solution like cyanide.

Many years ago we thought we had shown that porosity was formed during simultaneous dissolution of FeNi in HCl solution, and we made a link with Cl-SCC of stainless steels. I still believe that, although the papers were not very convincing.[5]

1 H. W. Pickering, *Corros. Sci.*, 1983, **23**, 1107.
2 I. C. Oppenheim, D. J. Trevor, C. E. Chidsey, P. L. Trevor and K. Sieradzki, *Science*, 1991, **254**, 687.
3 F. U. Renner, A. Stierle, H. Dosch, D. M. Kolb, T.-L. Lee and J. Zegenhagen, *Nature*, 2006, **439**, 707.
4 J. Erlebacher, *J. Electrochem. Soc.*, 2004, **151**, C614.
5 R. C. Newman, R. R. Corderman and K. Sieradzki, Evidence for de-alloying of austenitic stainless steels in simulated stress corrosion crack environments, *Br. Corros. J.*, 1989, **24**, 143–148.

Gerald Frankel said: Others have shown that the semiconducting properties on the passive film on Alloy 800 are a function of the thiosulfate concentration.[1] This behavior correlates with the pitting behavior. In a sense, your measurements are also correlations. How can you rule out the impact of the passive film?

1 J. Luo, personal communication.

Roger Newman responded: I don't know what is meant by correlation in the case of the semiconducting properties. I have seen work of this type where thiosulfate was used, but as I recall (and it may not have been the work of Luo), the authors ignored the framework that we set out in the 1980s. There are many elements of that framework, but the two most important ones are (1) that pitting occurs (with chloride and thiosulfate) at potentials way below where it would ever occur with only chloride, and (2) that pitting occurs in mixtures of sulfate and thiosulfate, but would never occur, at any potential, with only sulfate. I don't know how a "correlation" based on semiconductor properties can accommodate either of these observations, which it would need to do to make any progress at all.

Philippe Marcus asked: Do you have any direct evidence that pitting can be initiated with sulfate/thiosulfate without chlorides (or is scratching necessary to depassivate the surface)? In work we did on FeCr alloys[1] we showed that when both chlorides and thiosulfates are present, passivity breakdown is caused by chlorides and then repassivation is precluded by adsorption of sulphur.

1 C. Duret-Thual, D. Costa, W. P. Yang and P. Marcus, The role of thiosulfates in the pitting corrosion of Fe-17Cr alloys in neutral chloride solution: Electrochemical and XPS study, *Corros. Sci.*, 1997, **39**, 913–933.

Roger Newman replied: It does initiate eventually if you just leave the sample in the susceptible range of potential – that's one reason why we apply an initial passivation in pure sulfate solution (the other reason is that we want a nice low baseline current when we scratch). It does take longer to initiate than when we have thiosulfate and chloride, which can be studied using ordinary voltammetry.[1]To study the sulfate–thiosulfate pitting using voltammetry requires an extremely low scan rate.

I would emphasize (and this is very important) that sulfate–thiosulfate pitting occurs at potentials that are far lower than where ordinary chloride pitting occurs.

Of course we don't know how much of the above is affected by particulate in the alloy, or surface roughness. It may be useful to compare the chloride–thiosulfate and sulfate–thiosulfate systems using very clean alloys, to see if the difference in initiation rate between chloride and sulfate increases. Choice of surface finish(es) would be important in such experiments. It is possible that the sulfate–thiosulfate pitting (or for that matter chloride–thiosulfate pitting) may vanish on surfaces that are extremely smooth and particle-free (see my response to Trevor Rayment for a comment on sputtered thin films and the absence of pitting above a certain Cr content).

1 R. C. Newman, H. S. Isaacs and B. Alman, Effects of sulfur compounds on the pitting behaviour of type 304 stainless steel in near neutral chloride solutions, *Corrosion*, 1982, **38**, 261–265.

Dirk Engelberg asked: I've noticed that all tested microstructures were in the solution annealed condition, which is different to how these alloys are used in plant (*e.g.* thermally treated – TT). Would you expect an effect of microstructure on pit nucleation behaviour and frequency? For example, how would the presence of carbides change the lower/upper bounds of pitting in Table 3/Figure 4?

Roger Newman answered: We use solution annealed alloys because we don't want to be distracted by microstructure effects – our interest is in the solid solution. Regarding the TT treatment, I recall we did a few experiments where we found easier pitting, probably because the Cr depletion is not completely eliminated –perhaps the Cr level next to the grain boundary is still 1 or 2% below the bulk alloy. It might be interesting to pursue that further. For mill-annealed alloys the depletion may be less. But certainly one should pay attention to microstructure in any such study dealing with real plant experience, as we sometimes do – in Canada we still have steam generators with Alloy 600 tubing that is sensitized. One way to preserve that tubing is to reduce secondary-side exposure to oxygenated water during plant outages, as that can contain reduced sulfur species from sludge.

Trevor Rayment commented: This is a question for Roger Newman and Philippe Marcus.

There has been a long standing debate in the corrosion community concerning the mechanism by which molybdenum confers protection against pitting. A simple, if not simplistic, summary of the two schools of thought is a follows. The first school (Philippe Marcus) proposes that the role of Mo is to make the passive film more resistant to pitting, whereas the second school (Roger Newman) proposes that the role of Mo is upon dissolution kinetics after initiation of pitting has taken place.

The debate over the mechanism(s) of pitting protection of molybdenum is not resolved but there has been no discussion of this important topic within this meeting yet. A great deal of experimental data has been published but it does not seem to have convinced all parties to the discussion. A Faraday meeting presents an ideal forum for such a debate.

Therefore I would like to ask Roger and Philippe to propose experimental evidence (new experiments) that others could provide which would persuade them to change their mind on the mechanism for molybdenum protection in corrosion.

Roger Newman answered: I believe many of the critical experiments have been done already. The problem, from where I stand, is that a long list of phenomena in pitting are nicely accounted for (and in several cases quantitatively) by a modified Galvele type of model.[1] Similar success was achieved in studies that addressed the effects of bromide, thiosulfate, temperature, *etc*. The only thing missing from this long list of successes is that (almost always) our definition of pitting was stable pitting. If one's definition is "first onset of detectable current transients due to passive film breakdown," then indeed there is some evidence that thiosulfate takes advantage of spontaneous breakdown events, detectable at the nA level in pitting experiments. But these (perhaps chloride-induced) events are still pits – quite large actually. Burstein and his students looked down to the pA level and found what they considered to be a different type of event, due perhaps to salt forming under the passive film and bursting it open.[2] I don't recall whether the frequency and potential dependence of such events was compared in steels with and without Mo. Such data (although the charges under the transients were still substantial in terms of number of atoms dissolved) may be valuable in determining whether or not Mo affects the nucleation frequency of relevant events. I also don't know whether or not the Burstein type of event occurs, or occurs with different frequency, in steels with lower particulate content than commercial steels. Such delicate experiments have not been done, as far as I know, in support of the "passive film breakdown" hypothesis.

One observation that may address whether the passive film controls pit initiation was that of Ryan *et al.*[3] Pitting vanished above a critical Cr content of the alloy, even under very aggressive conditions. However our interpretation was as follows – these alloys were very smooth, and extreme current densities would be required to initiate any kind of pit. However below the critical Cr concentration, initial dissolution proceeded into the alloy along Fe-rich paths, creating the necessary occlusion for pit nucleation and bringing the observations back into the "Galvele" fold.

The sulfate–thiosulfate pitting is addressed in my response to Dr Marcus. One issue here is that we do not know whether the pitting that we studied (in commercial or home-made alloys) was related to second-phase particles.

1 N. J. Laycock and R. C. Newman, Localized dissolution kinetics, salt films and pitting potentials, *Corros. Sci.*, 1997, **39**, 1771–1790.
2 S. P. Mattin and G. T. Burstein, *Philos. Mag. Lett.*, 1997, **76**, 341.
3 M. P. Ryan, N. J. Laycock, R. C. Newman and H. S. Isaacs, The pitting behavior of Fe–Cr thin film alloys in hydrochloric acid, *J. Electrochem. Soc.*, 1998, **145**, 1566–1571.

Philippe Marcus answered: My response to this question is in three points:

(1) Role of the passive film in protection against pitting.

The role of the passive film in preventing or retarding pitting initiation is extremely important. Indeed it has been demonstrated that on the same alloy and in the same solution enhanced pitting protection is obtained by ageing in the solution, and that this is related to modifications of the chemical composition of the passive film.[1]

An experiment that could contradict the above observation and conclusion would be an experiment in which a well controlled change of composition and structure of the passive film produced on the same alloy and in the same solution would change nothing in the pitting initiation (pitting potential and time to initiation).

(2) Role of molybdenum in both pitting protection by a passive film containing molybdenum, and dissolution kinetics after pitting initiation.

There is no reason to exclude that molybdenum plays both roles, and indeed I think that Mo has two effects: it acts in the passive film resistance against pitting initiation, as well as in the dissolution kinetics after initiation of pitting.

The former effect is likely provided by Mo^{6+} locally enriched on the passivated surface[2] and the latter effect is provided by Mo in the alloy slowing down the dissolution kinetics in the active state (an effect clearly observed in comparing the dissolution kinetics in the active state of 304 and 316 stainless steels, or ferritic stainless steels without and with molybdenum, see *e.g.* Marcus and Olefjord.[3]

(3) Another beneficial effect of molybdenum, originally shown for nickel alloys,[4] is that Mo located on the surface binds to adsorbed sulfur and removes it from the surface (by dissolution), thus improving the corrosion resistance when sulfur species are present.

1 W. P. Yang, D. Costa and P. Marcus, Chemical composition, chemical states, and resistance to localized corrosion of passive films on an Fe–17%Cr alloy, *J. Electrochem. Soc.*, 1994, **141**, 111–116.
2 Vincent Maurice, Hao Peng, Lorena H. Klein, Antoine Seyeux, Sandrine Zanna and Philippe Marcus, *Faraday Discuss.*, 2015, DOI:10.1039/c4fd00231h.
3 P. Marcus and I. Olefjord, A round robin on combined electrochemical and AES/ESCA characterization of the passive films on Fe–Cr and Fe–Cr–Mo alloys, *Corrosion Science*, 1988, **28**, 589–602.
4 P. Marcus and M. Moscatelli, The role of alloyed molybdenum in the dissolution and the passivation of nickel–molybdenum alloys in the presence of adsorbed sulphur, *J. Electrochem. Soc.*, 1989, **136**, 1634–1637.

John Scully enquired: Operating on the assumption that the pitting potential reflects ease of initiation and stabilization with perhaps more weight on stabilization, are there examples where the oxide plays a big role in initiation and thereby affects the pitting potential? In relatively defect free materials, could emphasis shift towards the oxide? One observation has been in the case of amorphous glasses and high purity or relatively defect free stainless steels that there are very few initiation events detected at the instrument limit. These alloys enjoy very high pitting potentials and it seems that the first “detected pit” immediately stabilizes pitting. This stands in contrast to garden variety stainless steels and aluminum alloys with many inclusions and intermetallics where there are many initiation events. You have mentioned that if the defect is on the order of the oxide thickness then stabilization would require extraordinary anodic currents and I agree. But, what was the atomistic event that led to rupture of the oxide in the first place and is oxide engineering then a fruitful avenue for research in relatively defect free materials?

Roger Newman answered: My main point is that the standard of proof is very high if one wants to attribute an improvement in pitting resistance (by alloying) to an increased resistance to passive film breakdown, other parameters such as surface finish and inclusion population, nature and size being kept constant. I don't know of any instance where that standard has been met, whereas for “dirty” alloys, the Galvele type of approach meets it routinely. You are asking whether for clean and/or specially formulated alloys the film might start to dominate and could be engineered for resistance to breakdown. One response to that would be to note that if pitting is not eliminated completely, the pits that do initiate will grow rapidly – this is like “dangerous” inhibition. That is why I would prefer to see passive films engineered to reduce the rate of the cathodic reaction – this is like “safe” inhibition. Assuming that in some applications the oxide could be appropriately engineered on a very clean and smooth substrate (and one would have to consider joining of the material, oxidation, surface damage, surface cleanliness, plastic deformation, *etc.*), I have no doubt that the nucleation frequency of pitting could be kept very low. We saw that ourselves in stainless steel thin films prepared by ion-assisted ion-beam sputtering (see Ryan citation in another answer). Of course that is a kind of coating, so one might more logically see improvement *via* the oxide route as something to pursue using advanced vacuum coating technology applicable to large components. As you know, such considerations apply differently to iron-base and aluminum-base systems, so there is no commonality across the range of our usual materials that suffer from pitting. It has been shown that thin-film aluminum contaminated by oxygen has very high pitting resistance[1] – one might consider this to be some kind of film-reinforcement effect, but I personally consider that this oxygen-alloying effect can be accommodated within a reaction-transport type of picture wherein oxygen dissolution into a proto-pit consumes acid.

[1] G. S. Frankel *et al.*, *J. Electrochem. Soc.*, 2014, **161**(4), C195–C200.

Dirk Engelberg opened a general discussion of the paper by Steven Street: For your time-lapse imaging experiment (Fig. 4) do you expect a change in relative humidity over time? Do you take the sample out of the humidity cabinet, and is there then enough time to equilibrate the environment before you take the next images?

Steven Street replied: Samples were in humidity controlled desiccators with clear glass lids through which observations can be made, so there was no exposure to the lab atmosphere during measurements. The time taken to take the image was about 1 min, and the contents of the desiccator helped buffer the temperature so there was little variation here. A Lascar data logger collecting both RH and temperature shows no substantial change in either during optical measurements, maintaining temperature within 3 °C and RH within 3%.

Geraint Williams asked: What role does differential aeration play in the pitting corrosion of the 304 observed under a magnesium chloride containing water droplet? For example, if the surface were to be fully immersed in an aqueous solution of equivalent concentration, would spontaneous pitting still be observed. Is there a lower threshold magnesium chloride concentration observed under a droplet for spontaneous pitting in the absence of external polarisation, than when the surface is fully immersed?

Is there any evidence that local alkalinity at the circumference of the droplet causes precipitation of magnesium hydroxide in the region? Maybe this would explain the ring of apparent metal excavation at the periphery of the droplet as shown in Fig. 4.

Finally, for droplets of different sizes, but fixed concentration, what parameter controls the rate of anodic dissolution? If the pit growth rate is a function of the area of solution in contact with the metal then this would indicate surface/cathodic control rather than there being any ohmic constraints.

Steven Street responded: As noted in another response, the fact that pits do not grow only in the centre of the droplets suggests that the entire surface is vulnerable to pitting initiation in thin droplets. We have started exploratory comparisons with full immersion experiments and have found pitting in concentrations similar to those maintained at the RH used in our atmospheric experiments. This work is in ongoing. Local alkalinity is thought to cause the precipitation of $Mg(OH)_2$ and possibly $MgCO_3$, pinning the droplet perimeter.[1] Figure 4 shows the perimeter of the pit, not the droplet, so we would expect the solution still be to quite acidic here. For fixed CDD and RH (concentration), increasing the droplet diameter tends to give a larger shallow dish diameter, as noted in another answer, so it is likely that this effect is due to the increasing area available for the cathode reaction. Similar increases with droplet size were observed by Mi *et al.*[2] Increasing CDD (*i.e*. droplet height) while maintaining droplet area and concentration also increases the corrosion rate (Fig. 3), which we believe is IR drop related, as discussed in the paper.

1 T. Tsuru, K. Tamiya, and A. Nishikata, Formation and growth of micro-droplets during the initial stage of atmospheric corrosion, *Electrochim. Acta*, 2004, **49**, 2709–2715.
2 N. Mi, S. M. Ghahari, T. Rayment and A. J. Davenport, Use of inkjet printing to deposit magnesium chloride salt patterns for investigation of atmospheric corrosion of 304 stainless steel, *Corros. Sci*. 2011, **53**, 3114–3121.

Gerald Frankel asked: In our work on corrosion of SS under droplets at low RH, the shallow pits smoothly transitioned into attack at smaller areas we called ears, which we attributed to cathodic limitations.[1] Why is that not a good explanation for your observations of pit morphology change?

1 Bastian Maier and G. S. Frankel, Pitting corrosion of bare stainless steel 304 under chloride solution droplets, *J. Electrochem. Soc.*, 2010, **157**, C302–C312.

Steven Street answered: The spiral shaped pits in this work are caused by the "earing" mechanism you described, and this should indeed have been clarified. We agree that the role solution thickness and cathodic current limitation is crucial to the development of these pits, which is supported by our observations of the effects CDD and conductivity (RH). We extended this approach to include the role of mass transport limitation, as we believe this is necessary in explaining the formation of satellite pits. It is interesting that you did not observe satellite pits, possibly due to a combination of slightly higher CDD and finer grinding of the metal surface, which would have removed occluded initiation sites that in our work led to satellites.

Dirk Engelberg asked: Is there interaction between satellite pits and the shallow dish/pit region, since the shallow region seems to have grown into satellite pits (*e.g*. Fig. 3 and Fig. 4)? (how does this affect cathodic *vs*. anodic regions?)

Steven Street answered: Evans' Droplet experiments on steel describe macroscopic general corrosion attack, not localised pitting corrosion. As such, they do not account for microstructure or inclusions common in stainless steel alloys. As Roger Newman pointed out, the model works on the basis of differential aeration which preferentially supplies edges of droplets with oxygen and promotes cathodic reactions there. The observation that usually only one pit is seen in a droplet is expected to be due to the drop in potential in the system associated with pitting. Under full immersion conditions, it is common to observe a sequence of metastable pits that show recovery of the potential after repassivation of previous pits.

David Williams said: I wonder about the temporal sequence of events in your experiments. Could it be that the shallow dishes form as a consequence of the activation of the surface near a pit by corrosion products (specifically sulfides or thiosulfates) that are diffusing out of an active pit? Such effects have been shown before.[1]

[1] D. E. Williams, T. F. Mohiuddin, Y. Y. Zhu, Elucidation of a trigger mechanism for pitting corrosion of stainless steels using submicron resolution scanning electrochemical and photoelectrochemical microscopy, *J. Electrochem. Soc.*, 1998, **145**, 2664–2672.

Steven Street responded: We don't doubt the importance of sulphide inclusions in pit initiation in these alloys, and there is a rich literature that supports this. In the discussion section of the paper we suggest that this is not the only factor controlling dish diameter since this varies with position in the droplet. In unpublished work, large droplets of 10 μl have consistently larger shallow dish regions with diameters exceeding 350 μm, and 100 μl droplets with shallow dishes of over 800 μm diameter. If sulphide is the controlling factor we would expect a small variation in dish sizes more similar to each other.

Cem Örnek commented: In 304L austenitic stainless steel the delta ferrite content is about 6–14%, depending on the microstructure processing orientation (TD, RD, ND). The ferrite has significantly different chemical composition in contrast to the austenite matrix which questions the role in localised corrosion. Furthermore, there are MnS and other non-metallic inclusions often present in the microstructure. How are these related to the corrosion morphology during atmospheric corrosion? Are there any preferential initiation sites observed? Can we say from selective corrosion? Can we speak about pitting corrosion if we see odd shaped corrosion morphologies?

Steven Street responded: Our steel contains ~4% delta ferrite, most of which is below the plate surface. We have demonstrated that it influences pit propagation.[1] Our steel also contains sulphide and oxide inclusions which are known to be pit initiation sites. However we have not carried out a systematic study on the influence of different initiation sites.

[1] A. J. Davenport, L. Guo, N. Mi, H. Mohammed-Ali, S. M. Ghahari, S. R. Street, N. J. Laycock, T. Rayment, C. Reinhard, C. Padovani and D. Krouse, Mechanistic studies of atmospheric pitting corrosion of stainless steel for ILW containers, *Corros. Eng.*, *Sci. Technol.*, 2014, **49**, 514–520.

Cem Örnek asked: Evans introduced the atmospheric corrosion model under thin-film electrolytes formed by a hemispherical water droplet. Thus the anode is primarily located in the centre of the droplet due to rapid oxygen depletion and impeded oxygen supply and the periphery of the droplet forms the cathode due to the excessive and quick access of oxygen. Preferential corrosion would be expected to occur at or close to the centre due to the development of a large net anodic potential. However, the results shown (and the poster from Angus Cook, University of Birmingham) clearly contradict the model of Evans. Research on the atmospheric corrosion behaviour on the same material and on 2205 duplex stainless steel by my humble self can confirm your observed results. However, there is no clear explanation given as to why the corrosion initiation occurs mostly between the centre and the peripheral area of a hemispherical chloride-containing droplet. Furthermore, the initiation of corrosion is concentrated on a confined region, and, usually, only one or a few corrosion pits are observed which is significantly different to corrosion initiation sites under immersed conditions.

Is there an explanation for this? By the way, corrosion was also observed occurring on the peripheral area and also on secondarily spread chloride regions.

Roger Newman replied: I don't believe the situation is as tidy as the Evans experiment. There are two major differences. First, the stainless steel is spontaneously passive, while the iron is spontaneously active. In the Evans experiment it is the alkalization at the periphery of the drop that passivates the iron and creates the active–passive couple. In the stainless steel experiment there is pit initiation and propagation, which is very different. Second, oxygen reduction on stainless steel is normally activation controlled, except where the stainless steel is in the active state, while in the Evans experiment oxygen reduction is diffusion-limited. As I indicated in another answer, oxygen reduction on stainless steel can also show apparent “limiting current densities” that are too low to be diffusion-limited in the electrolyte.

Roger Newman commented: The reference to Evans' famous drop experiment (on iron) may not be appropriate if oxygen reduction on stainless steel is kinetically rather than diffusion limited. In the drop experiment, oxygen reduction is everywhere under diffusion control.

As a footnote to this comment, it might be interesting to vary the partial pressure of oxygen over the experiment, or in some other way to probe the status of the oxygen reduction reaction.

An old observation is that oxygen reduction on stainless steel sometimes appears to be mass transfer limited, but the limiting current density is too low for boundary-layer diffusion. In that case something within the passive film itself is limiting the reaction. Someone must have explained this.

Steven Street answered: Thank you for your very interesting comments. A further brief discussion on Evans’ droplet model has been addressed in answer to another question.

Dirk Engelberg asked: Can you suggest a viable corrosion mitigation strategy to prevent localised corrosion in this system (since you show pitting corrosion occurs with exposure to deliquescence relative humidity, and increasing the relative humidity (*e.g.* 56%) also results in pitting corrosion). Do you accept a chloride deposition density of 10 μm cm^{-2} as a working threshold or have you observed corrosion occurring below this threshold? Can you speculate whether a change of shape during pit growth can be used to affect (and control) pit growth kinetics?

Steven Street responded: The obvious solution is to try to keep chloride concentrations as low as possible and to limit the thickness and continuity of the electrolyte layer. An alternative method would be maintaining a very high RH in storage, to ensure any salts that do deliquesce remain dilute, but these would necessarily pass through an initial highly concentrated stage which may cause corrosion, if only superficially. As initiation sites are seen to not reinitiate pitting once passivated, natural wet–dry fluctuations could be used to exhaust these sites on the surface of the alloy.[1] An improved alloy, such as 316L, would certainly improve performance. 10 μm cm^{-2} CDD is significantly lower than the values used in this paper. A recent study[2] suggests that there is merit to the use of a working threshold.

1 A. J. Davenport, L. Guo, N. Mi, H. Mohammed-Ali, S. M. Ghahari, S. R. Street, N. J. Laycock, T. Rayment, C. Reinhard, C. Padovani and D. Krouse, Mechanistic studies of atmospheric pitting corrosion of stainless steel for ILW containers, *Corros. Eng.*, *Sci. Technol.*, 2014, **49**, 514–520.
2 C. Padovani, R. J. Winsley, N. R. Smart, P. A. H. Fennell, C. Harris and K. Christie, Corrosion control of stainless steels in indoor atmospheres? Practical experience (Part 2), *Corrosion*, 2015, **71**, 646–666.

David Williams asked: I wonder if there are any convection effects associated with surface tension gradients developed as droplets evaporate? Thus, are there any effects that are different at the centre compared with towards the edge of the droplet?

Steven Street replied: Convection effects are something we did not consider and perhaps should have, as the droplet loses up to 95% of its initial volume as it equilibrates with RH within the first hour. We show in Figure 8 that the diameter of the shallow dishes are greater in the centre of the droplet. We attribute this to an increased IR drop and mass transport limitations at the edges. We do not observe any other effect that might be attributed to convection.

Siaw Foon Lee communicated: Under the section of “Experimental”, third paragraph – Arrays of 2 μl droplets of 0.27 M $MgCl_2$ were deposited…and Fig. 1(a) showing the relationship between the solution concentration (M) of $MgCl_2$ and relative humidity (%). My question is that could the author shows the calculation steps of how to convert 2 μl droplets of 0.27 M $MgCl_2$ to 5M $MgCl_2$ after it was held in an ECO135 atmospheric chamber for 24 h with the humidity of 33%?

Steven Street communicated in reply: The concentration of the solution is determined by its water activity as it reaches equilibrium with the relative humidity. At equilibrium, the water activity in the air and water phases are equal, regardless of the initial solution concentration. The calculations of equilibrium concentrations are based on Figure 1(a) which was calculated using OLI Systems.

Siaw Foon Lee communicated: Table 2 – the humidity of 33% has a droplet area on deposition of 0.048 cm^2 and has an average droplet CDD of 80 μg cm^{-2}. The humidity of 43% has a droplet area on deposition of 0.048 cm^2 that is same as that of the humidity of 33%, however, it has an average droplet CDD of 790 μg cm^{-2}. I am curious to know how the author works out the calculation since this topic is new to me.

Steven Street communicated in reply: Chloride deposition density is an average measure of mass of chloride over a defined area, in this case the area of the droplet. In our experiments, CDD was altered by varying the deposition solution concentration. As noted in the paper (Table 2) the droplet areas are measured at deposition, as droplet spreading can occur during atmospheric corrosion.

Siaw Foon Lee communicated: Under the section of “Experimental,” subsection of “Electrochemical sweeps,” second paragraph, starting from the second line. The solutions used were de-aerated by bubbling argon for 20 min…” Could I know about the minimum oxygen concentration of the electrolyte the author achieved using this method? Can the oxygen concentration remain the same during the experiment using this method?

Steven Street communicated in reply: Oxygen concentration was not measured in this experiment. Checks on similar measurements on oxygen reduction rate on Pt wire suggest that this method can maintain concentration.

Dirk Engelberg opened a general discussion of the paper by V. Vivier: Do you keep your micro-capillary very close to the surface (10–15 microns) to initially generate a "crevice-type" environment to induce pitting (crevice)? Do you try to keep the condition (in particular the chloride concentration) in this confined space below the capillary stable during the experiments?

Stephane Heurtault answered: The proximity of the micro-capillary to the stainless steel surface, together with the chosen chloride concentration in the syringe and the release flow rate, helps to create an appropriate environment for pit initiation and propagation. The distance between the micro-capillary and the stainless steel surface was selected to produce a single pit on the steel. 15 microns is the highest distance fulfilling this condition. The chloride concentration injected by the micro-capillary does not necessarily have to be constant during the propagation phase. The supply of chloride has only to be greater or equal to the critical chloride concentration determined in part 3.3.2 of this article.

As you mention crevices, it is well known from the literature that crevices can develop from pits. However after 1 h of propagation, a pit cross section performed in our pit did not show any crevice.

Alison Davenport remarked: Have you carried out a systematic investigation to determine whether the flow rate of the solution influences pit growth? Some of your pits appear to have broken covers: were they damaged during the experiment or afterwards during transfer to the SEM?

Stephane Heurtault replied: The flow rate of the solution is one of the main parameters for the supply of chloride in the environment and it influences the pit growth. The supply of chloride (in mol h^{-1}) can be defined as the product of chloride concentration (in mol L^{-1}) and flow rate (in L h^{-1}). However, we have shown that we can control the amount of chloride independently by changing the chloride concentration or by modifying the flow rate (see for instance the results presented in Fig. 5). With a chloride flow rate of 5.4 μL h^{-1} (as used in most of our experiments presented in this paper) and taking into account the evolution of the pit volume plotted in Fig. 10, only 3 min are required to renew entirely the pit solution after 1 h of propagation, and it will take 30 min after 10 h of propagation. Thus, the convection induced by the micro-capillary may be an important factor that controls the pit propagation. To avoid such a behavior, it is possible to generate and to propagate the pit in two successive steps: first, the pit is generated beneath the micro-capillary and then, it is sustained by controlling the bulk concentration in chloride as was shown possible in the last part of the article.

We believe that the pit cover shown in Fig. 6(a) was not damaged during the experiment but afterwards during transfer to the SEM. Indeed, in another experiment, we succeeded in obtaining a no-broken pit cover using the same experimental conditions. Nevertheless it is possible to break the pit cover during the experiment, for example performing an anodic potential change during the propagation.

Roger Newman asked: Why do you use such a strong sulfate solution? It seems that complications from the mixing of chloride and sulfate could be minimized if you just reduced the sulfate concentration by a factor of 10. Some of your experiments where you vary the chloride might be affected by varying degrees of inhibition by sulfate (since inhibition is related to the chloride/sulfate ratio).

Stephane Heurtault replied: We used such a strong sulfate concentration to be sure that the solution conductivity is high enough, but we know that it affects the pit growth. In our previous work,[1] differences between sulfate and perchlorate solution were investigated. Moreover, some experiments were performed using 6 M SO_4^{2-} and 1.2 M Cl^- instead of 0.5 M SO_4^{2-} and 1.2 M Cl^-. With this increase in sulfate concentration (corresponding to a decrease of the chloride to sulfate ratio), the inhibitor role of sulfate was shown. We agree with this comment that the chloride to sulfate ratio is an important point instead of only indicating the chloride concentration.

[1] N. Aouina *et al.*, *Electrochim. Acta*, 2013, **104**, 274.

Gerald Frankel stated: You show that the depth varies with $t^{0.5}$, which would also be found for ohmic control. How can you rule out ohmic effects?

Stephane Heurtault answered: Indeed it should have been mentioned that the variation of pit depth with $t^{0.5}$ also accounts for ohmic control as shown previously.[1] The same dependence with time of pit depth for both ohmic control and diffusion complicates the data interpretation. However for a pit under diffusion control, potential variation has no effect on the pit growth rate, whereas a pit growing under ohmic control depends on potential according Ohm's law. Additional experiments at 20 °C injecting 3 M NaCl + 0.5 M H_2SO_4 with the glass microcapillary were performed by changing the electrode potential during the pit propagation (data not shown in this paper). The single pit was initially formed at 0 V/MSE. After 1 h of propagation, the potential was changed to 0.4 V/MSE. Then the pit depth with this modification of potential was measured and the current density at the pit bottom after changing the potential was calculated using equation (5). It was shown that the modification of potential does not affect the calculated pit bottom current density, indicating a diffusion-control process.

[1] G. S. Frankel, *J. Electrochem. Soc.*, 1998, **145**, 2186.

David Williams commented Laycock *et al.* have given a rather complete computational model for evolution of pit shape, including the perforated covers.[1,2] Have you been able to compare your results with such a model? Also, have you been able to see the current fluctuations that should result as the perforations in the pit cover develop? Pit 'death' happens when the cover is detached and the internal processes cannot sustain the critical solution composition against the resultant increased flux out of the pit. This is usually indicated by a sharp increase of current followed by an immediate fall to zero (*e.g.* ref. 3). Have you been able to see such effects in your experiments?

1 N. J. Laycock, S. P. White, J. S. Noh, P. T. Wilson and R. C. Newman, Perforated covers for propagating pits, *J. Electrochem. Soc.*, 1998, **145**, 1101–1108.
2 N. J. Laycock and S. P. White, Computer simulation of single pit propagation in stainless steel under potentiostatic control, *J. Electrochem. Soc.*, 2001, **148**, B264–B275.
3 D. E. Williams, J. Stewart and P. H. Balkwill, The nucleation, growth and stability of micropits in stainless steel, *Corros. Sci.*, 1994, **36**, 1213–1235.

Stephane Heurtault responded: The Laycock model is a great advancement in our understanding of pitting propagation on stainless steel. This model was devised for a disc-shaped pit and accounted for the presence of a salt film at the pit bottom. Due to this salt film, an additional potential drop at the pit bottom exists, which implies a lower current density beneath the salt film than at the pit edges. These results are fully consistent with our experiments (disc-shaped pit and salt film at the bottom of the pit). The Laycock model also accounts for the presence of a pit cover, which is composed of a central hole surrounded by many small perforations forming the lacy-like structure. According to the model, the cover entirely dissolves for long-term pit propagation. In our experiments, using the adequate chloride concentration injected by the micro-capillary, we can get single pits which propagate without any pit cover (this is possible according to the Laycock model) or we can also observe the propagation of a single pit with cover. However, the pit cover obtained in our experiments has only a central hole at the location corresponding to the chloride solution injection by the micro-capillary, and only one or two perforations can be observed in the periphery. This specific behavior may be explained by the presence of the micro-capillary above the pit maintaining the concentration of chloride ions at a high level. We didn't see any current fluctuations resulting from the perforations of the pit cover. This was confirmed by SEM observations. However for both covered and uncovered pits, we noticed small current oscillations which can probably be ascribed to the growth and the breakdown of a thin oxide layer under the salt film.[1,2]

Once the pit propagates, we have never observed repassivation after the collapse of the pit cover. However, it should be mentioned that an increase of the electrode potential during the pit propagation was accompanied by the collapse of the pit cover. In that case, the current increased sharply during the collapse, but the propagation was maintained.

1 R. C. Newman and M. A. A. Ajjawi, *Corros. Sci.*, 1986, **26**, 1057.
2 N. J. Laycock and R. C. Newman, *Mater. Sci. Forum*, 1995, **192**, 649.

Alison Davenport commented: We have recently carried out some radiography work on the growth of 2D pits in stainless steel foils.[1,2] We also found out that growth rate at the bottom of the pit is slower than the sides of the pit. We also attribute this to diffusion-controlled growth of the pit bottom. However, in the presence of a perforated pit cover, the solution concentration at the pit mouth will not be zero as the cover provides an additional diffusion barrier. We found that the growth of the pit width is under ohmic control as the rate increases with solution conductivity.

1 M. Ghahari, *In Situ* Synchrotron X-Ray Characterisation and Modelling of Pitting Corrosion of Stainless Steel, *PhD Thesis*, University of Birmingham, 2012, http://etheses.bham.ac.uk/3269/11/Ghahari12PhD.pdf.
2 M. Ghahari *et al.*, *Corros. Sci.*, submitted.

Alison Davenport opened a general discussion of the paper by David Shoesmith: What are the most effective ways to simulate the effect of radiation on corrosion of UO_2 under realistic conditions?

David Shoesmith answered: A number of experimental approaches can be used.

(a) For γ-radiolysis, direct exposure of the UO_2 to a gamma field with a calibrated dose rate can be used.

(b) For α-radiolysis, UO_2 specimens doped with α-emitters (*e.g.*, Pu(239), U(233)) to provide a known dose rate have been used.[1] This method provides an *in situ* α-radiation field.

(c) An alternative method for α-radiolysis is to use a thin layer electrochemical cell with the electrode (UO_2) brought close to a Au-coated α-source ($\nleqq$ 25μm) with a known dose rate.[2] This method provides an *ex-situ* source.

(d) Intense beams (*e.g.*, X-rays (Ross Springell *et al.*[3])) can be used, but usually produce extremely high dose rates well beyond those expected inside a failed container.

(e) The influence of γ-radiolysis (and also α-radiolysis) can be simulated by adding the anticipated concentration of hydrogen peroxide chemically. Evidence in support of this approach is well documented.[4]

1 M. Broczkowski *et al., ACS Symposium Proc.*, 2010, **1046**, 34–380.
2 J. C. Wren *et al.*, *J. Electrochem. Soc.*, 2005, **152**, B470–B481.
3 Ross Springell, Sophie Rennie, Leila Costelle, James Darnbrough, Camilla Stitt, Elizabeth Cocklin, Chris Lucas, Robert Burrows, Howard Sims, Didier Wermeille, Jonathan Rawle, Chris Nicklin, William Nuttall, Thomas Scott and Gerard Lander, *Faraday Discuss.*, 2015, DOI:10.1039/c4fd00254g.
4 J. C.Wren, *ACS Symposium Proc.*, 2010, **1046**, 271–295.

Ross Springell replied: Simulating the effects of corrosion of UO_2 under realistic conditions initially requires one to define what these conditions might be, and this can depend on what scenario you choose. The most frequently used method is the addition of small quantities of H_2O_2 to the aqueous environment. This is based on the assumption that any container of spent nuclear fuel will likely fail after the first few hundred years when the gamma fields from the fission products have decayed and the dominant radiation fields are driven by alpha decay; in this case the dominant radiolytic product will be H_2O_2. However, the most likely cause of any containment failure is due to potential defects in the vessel weld. This will be present from day 1 and it is possible that water may ingress way before all of the fission products have decayed. In this instance, strong gamma fields will also be present and this will result in both H_2O_2 and other more oxidising free radicals at the fuel surface. A lot of this discussion really depends on the precise packaging methods and eventual repository conditions. One method to better simulate the radiation fields would be to study changes in the UO_2/water interfaces exposed to an alpha source and a gamma source, but these would have to be *ex-situ* studies with characterisation of the structure with

X-rays at a later time. The advantage of the experimental method outlined in this paper is that we are able to probe the structural changes *in situ*.

John Scully asked: Could you comment on the number of adjustable or disposable parameters that a model like this has, or should be limited to? Of course, it seems that corrosion science might work to define as many "unit processes" as possible so as to eliminate some adjustable parameters when they can be replaced. Is this your view too, or do you see another way forward?

David Shoesmith answered: The primary basis of a model like this one (fuel corrosion model) is a mechanistic understanding of the key reactions required to describe the corrosion process. Our guiding principle is that the model should contain the minimum number of reactions necessary to reasonably represent the overall process. To achieve this the model should contain the minimum number of adjustable or disposable parameters. Ideally, the model should then yield output values which can be compared to trusted experimental data. Unfortunately, required data is commonly not available, unreliable, or determined for inappropriate conditions. Disagreement between calculated (model) and measured values can, however, provide a template for required measurements or theoretical calculations.

Unfortunately, models and calculations can be developed and performed on a time scale which cannot be matched by experimental determinations. This commonly leads to the "over-extension" of models beyond validation, either by comparison to measurements or by theoretical calculations. This is generally the reason for the use of adjustable parameters. The more such parameters are included the more over-extended and unreliable the model becomes. Such over-extensions should be minimized by the iterative process of the model (often sensitivity) calculations, experimental determinations, model redevelopment.

Alison Davenport asked: Could you give further details on the uncertainty in the input parameters to the model, and to the sensitivity of the model to different parameters? Are there any input parameters for which improved measurements would be helpful to reduce the uncertainty in the model?

David Shoesmith responded: There are many uncertainties in the input parameters to the model in its present form. The mechanistic basis is reasonably well established although a detailed understanding of how hydrogen peroxide reacts and interacts with hydrogen on the UO_2 surface has proven elusive. The key uncertainties are in the values of the rate constants required, many of which are uncertain and some of which are unknown. The sources and uncertainties of the input parameters have been discussed elsewhere.[1–3]

The key uncertainty encountered is in the justification that parameter values measured in experimentally accessible concentration ranges can be used in the concentration ranges anticipated inside a failed container which are orders of magnitude lower. Additionally the model cannot be considered fully developed in its present form. While the goal is to develop a transparent and readily comprehensible model with as few complexities as possible, a number of features remain to be elucidated. These include the possibility of corrosion product deposition, especially within fuel fractures. Their presence will lead to uncertain diffusion fields between the two corrosion fronts within the container. The consequences of various failure modes of the fuel cladding is also not included. Model validation is also an on-going issue, and an attempt to compare model calculations to natural analogs is being made.

1 L. Wu, Y. Beauregard, Z. Qin, S. Rohani and D. W. Shoesmith, *Corros. Sci.*, 2012, **61**, 83–91.
2 Linda Wu, Zack Qin and David W. Shoesmith, *Corros. Sci.*, 2014, **84**, 85–95.
3 Linda Wu, Nazhen Liu, Zack Qin and David W. Shoesmith, *J. Electrochem. Soc.*, 2014, **161**, E3259–E3266.

Christopher Taylor asked: Early in the presentation you mention the hypothesis or expectation that the epsilon particles, being noble, could drive anodic processes by acting as a cathodic electron sink by catalyzing HER. However, it appears that instead, your expectation is that they will have an opposite effect, by quenching H_2O_2. Is this the correct interpretation of the role of epsilon particles, or does the competition between these two effects still need to be elucidated?

David Shoesmith responded: We are studying these reactions extensively and many features remain to be elucidated. We have good experimental evidence that these particles act as cathodes to reduce hydrogen peroxide (in the absence of hydrogen), as anodes to oxidize hydrogen (in the absence of hydrogen peroxide), and as a catalysts on which hydrogen oxidation and hydrogen peroxide reduction can couple to yield water. It is this last reaction which can consume hydrogen peroxide and prevent it from driving uranium dioxide corrosion. To date we have not been able to quantitatively determine the kinetic relationships describing these reactions although we have some preliminary data. There are a number of unresolved issues. We do not know the kinetics of hydrogen peroxide decomposition (to oxygen and water) which model sensitivity calculations tell us are important. The influence of alpha radiolysis in "hidden" locations (deep cracks, grain boundary tunnels) is underway but incomplete, and the relative importance of the noble metal particles and the uranium dioxide surface in hydrogen peroxide reactions is uncertain. I could extend the list!

Ross Springell said: You mention in your article that UO_2 has the potential to have a catalytic effect that may influence its corrosion. Could you expand on this point and describe how important the stoichiometry is in this aspect?

David Shoesmith replied: Many oxide catalysts act as electron donor–acceptor catalysts especially p-type oxides.[1] This is attributed to the existence of adjacent metal ions with the surface ion being in a higher oxidation state (*e.g.*, U(V)) than that immediately below (U(IV)). This kind of catalysis is exhibited by Ce (III/IV) oxide. If such a catalysis occurs then an increase in non-stoichiometry (x in $UO_{(2+x)}$) would be expected to enhance catalysis. This effect has been proposed to explain the kinetics of hydrogen peroxide reduction on uranium dioxide.[2,3] However, it is a little more complicated than this and presently not totally resolved.

1 V. Presnov and A. M. Trunov, *Elektrokhimiya*, 1975, **11**, 77.
2 J. S. Goldik *et al., Electrochim. Acta*, 2004, **49** 1699.
3 J. S. Goldik, J. J. Noël and D.W. Shoesmith, *J. Electroanal. Chem.*, **582**, 2005, 241.

Angus Cook commented: In your model system of a failed nuclear waste container (Fig. 2) there is no accounting for any cladding material around the nuclear fuel.

How might cladding change this system?

David Shoesmith answered: Only the electrochemical and chemical reactions were included in the model presented. The Zircaloy cladding is expected to be chemically inert and not involved in the redox processes determining the UO_2 behaviour. Its effect will be as a separating barrier between the site of radiolytic oxidant production at the fuel surface and the site of Fe(II) and H_2 production at the steel container inner surface. It will, therefore, influence the diffusion processes and hence the ability of H_2 to control the redox conditions at the fuel surface by reaction with H_2O_2 and of Fe(II) to consume H_2O_2 by the Fenton reaction. Its efficiency in interfering with these reactions will be determined by the physical nature of the failure in the fuel cladding. We are presently trying to model this effect within our finite element model.

Dirk Engelberg said: With the presence of hydrogen peroxide in the aqueous phase, and/or catalytic reactions expected to occur at the uranium surface/particles (H_2/H^+) wouldn't you expect the formation of uranium hydride?

David Shoesmith answered: The fuel form is uranium dioxide not uranium metal. Hydride formation would only be expected if uranium in the zero oxidation state was present. While H atoms will form on the noble metal particles (an alloy of Ru, Pd and Mo), and some minor absorption into the particle may be possible, this will not lead to reduction of the U(IV) oxide to U metal.

Christopher Taylor remarked: For the water gas shift and reverse water gas shift research efforts, bifunctional catalysts that contain nanoparticles of precious or noble metals dispersed over a redox-active oxide, like ceria, are used to tune the reaction chemistry for $CO_2 + H_2 \rightleftharpoons CO + H_2O$ and potentially form hydrocarbon products. In your case, you have a similar set-up between these epsilon particles, which are noble and catalytic, and the redox active UO_2. By analogy, then we might expect the interfaces between the particles and the urania to be the active regions whereby CO_2 is able to engage in chemistry with the material. Are there other possible insights that could be gained by this analogy?

David Shoesmith responded: The analogy is a good one. In the reaction you describe on ceria you note that the whole oxide matrix is involved not just the dispersed noble metal nanoparticles, but you suspect the coupling within the uranium dioxide will be limited to regions close to the noble metal particles. I agree. The area of the reactive uranium dioxide influenced by the noble metal anode/cathode will be determined by the electrical conductivity of the rare earth doped oxide lattice and the ionic conductivity of the electrolyte it is exposed to; *i.e.*, this is a normal microgalvanic (or internal) coupling process.

I think the analogy can be extended in terms of the behaviour of the uranium and cerium oxides. The hydrogen peroxide we are interested in will react directly on the uranium dioxide surface besides *via* the galvanic coupling process, making the catalytic properties of the oxide also important. Both cerium oxide and uranium dioxide have the same lattice structure and uranium dioxide has the potential to act as a redox catalyst *via* similar mechanisms to those occurring on the much more extensively studied cerium oxide. It is well worth investigating whether this is the case and whether the tuning mechanisms for ceria that you refer to also occur on uranium dioxide.

Clara Wren opened a general discussion of the paper by Ross Springell: The concentration of the radiolytically-produced H_2O_2 that you quoted is very high at ~ 10^{-4} M. What was the energy absorbed by water? Can X-ray induced radiolysis create that high an H_2O_2 concentration? The photoelectrons generated in the UO_2 matrix should lose most of their energy to overcome the binding energy and work function, and, when they are ejected from the UO_2 matrix, will have a relatively low energy, on the order of ~ 100 eV. This is not sufficient to penetrate the adsorbed water layer but is sufficient to ionize water molecules close to the UO_2 surface, affecting the water chemistry close to the surface. If this is the case, the X-ray induced corrosion may be different from that driven by higher energy radiation such as gamma-rays. Can you comment on the potential differences arising in X-ray and γ-ray induced corrosion?

Ross Springell replied: The X-ray energy is 17 keV and for the average 0.5 mm coverage of water that we used in this experiment, the transmission was 59%, which means that 41% of the total photon flux (approx. 10^{12} photons s^{-1}) was absorbed in the beam track through the water. By using the linear energy transfer (LET) of X-rays at this energy it is possible to calculate the number of H_2O_2 molecules produced per 100 eV deposited, per photon. The high photon flux results in the increase of H_2O_2 concentration up to its equilibrium concentration within a fraction of a second. Both the X-rays and gamma rays have a similar LET and produce similar proportions of radiolytic product, but it is certainly the situation that the absorption in the water is much stronger for the X-ray case. In fact, it is this property that we rely on to enable us to measure the corrosion *in situ* during the time frame of a synchrotron experiment; in real spent fuel stores the rates of corrosion are considerably slower.

Geoffrey Thornton stated: We have recorded SXRD data (CTR's) from a water/TiO_2(110) interface using ID32 at the ESRF. The photon flux was also 17 keV, with a photon flux of 10^{12} ph s^{-1}. We see an interface ordered on the atomic scale. In other words, there is no evidence of beam damage. A key difference between your sample and the TiO_2(110) substrate is that the former employs an insulating substrate, whereas the latter was a self-doped n-type semiconductor. Hence, it may be a charging effect that gives rise to the beam damage you observe.

Ross Springell answered: The beam parameters described in the SXRD measurements on TiO_2 at ID32 are remarkably similar to our own, and it's surprising that no beam damage is observed at all. The possible charging of the YSZ insulating substrates as a potential cause of the increased rate of corrosion observed in the UO_2 films is a good suggestion and we will look toward a conducting substrate system in the future to test this theory.

Rob Lindsay commented: As you indicate in the paper, it is somewhat surprising that the (001), (110), and (111) UO_2 surfaces all exhibit similar dissolution rates. How well characterised are these surfaces? For example, have you employed STM to image them in real space? It may be that dissolution is dominated by loss of atoms from step edges or other ‘defect sites,’ and so rates are more similar than expected for the three surface orientations.

Ross Springell responded: To date our characterisation of the different surfaces has relied solely on X-ray diffraction techniques and in some cases high speed AFM. Diffraction spectra imply large regions with very low roughness (less than 2 monolayers), but in order to be certain of the surface morphology we will look to try a technique with much better real space resolution such as STM, as suggested. In order to further investigate the effect of crystal surface, we are planning an *in situ* high speed AFM study of the corrosion of a number of UO_2 crystal grains on a longer time-scale, using hydrogen peroxide as the oxidant.

David Shoesmith asked: Have you tried to characterize the UO_2 layer before exposure and the oxidized surface layer after exposure using techniques such as Raman spectroscopy and X-ray photoelectron spectroscopy?

Ross Springell responded: We have made some measurements of the oxidised surface layer after exposure, using X-ray photoelectron spectroscopy (XPS), mapping across a corroded region. Our first results indicate a more oxidised hyperstoichiometric surface into the corroded region and then potentially a higher uranium oxide in the very centre of the trough, due to redeposition of material out of the water, on drying. We have beam-time scheduled at I09, Diamond Light Source, to conduct a full investigation of the oxidation of these corroded regions *in situ*, using XPS. Raman spectroscopy is an excellent suggestion; although our films are too thin for this technique to be sensitive in this case, we plan to grow a series of much thicker films and measure the Raman spectra for a range of stoichiometries.

Philippe Marcus asked: Can we really implant in the human body a stent that would produce a lot of hydrogen? What is the conclusion in terms of the effect of iron impurity in magnesium on hydrogen evolution (one of the hypotheses included in the Introductory Lecture presented by Gerald Frankel[1] to explain the “anodic” hydrogen) and what are the implications for the application of Mg alloys for stents (requested purity of Mg)?

[1] G. S. Frankel, S. Fajardo and B. M. Lynch, *Faraday Discuss.*, 2015, DOI:10.1039/c5fd00066a.

Sannakaisa Virtanen replied: Certainly the hydrogen gas evolution by Mg based stents is of high concern. There are studies related to the fate of hydrogen gas in different types of *in vivo* situations. The danger of hydrogen gas generation in the biomedical application can be expected to depend on the temporal and spatial rate of its production: *i.e.*, sufficiently slow gas generation can be tolerated (gas can be transported away and local build-up of significant volumes of gas can be avoided). What is typically observed for Mg alloys in simulated *in vivo* conditions, for instance in cell culture medium (but NOT in more simple simulated body solutions, SBFs, which only mimic the inorganic components of blood and do not contain for instance amino acids), is that the initial production of hydrogen gas is quite strong, and in a relatively short time (in the first hours of immersion) the surface is "passivated" by formation of a protective corrosion product layer. Therefore, the key for a safe application from my point of view is to modify the alloy surface with a biodegradable coating, which only offers a weak barrier function, but reduces the initially too high reactivity of the Mg surface. Also, Mg alloy purity certainly is of very high importance in this field.

The corrosion challenge is not only related to hydrogen gas. Also local pH increase can be deleterious for the biological surroundings. But one should consider that most laboratory studies on Mg corrosion are performed under static conditions and this is far from the highly dynamic situation *in vivo*. So there is quite a lot still to do.

Geraint Williams responded: This point is well made. The majority of research devoted to bioresorbable Mg implants largely ignores the fact there may be problems which arise *in vivo* due to high local concentrations of hydrogen caused by corroding magnesium. Most attention has been concentrated on the biocompatibility of the cations which are released upon corrosion. Given the well documented influence of iron impurity level on corrosion rate, closely controlling the trace Fe content of Mg may provide a means of "tuning" the corrosion rate to one which lies in an acceptable time window for optimum *in vivo* performance. However, in reality the situation will be much more complicated since it is likely that nominally pure Mg, with a certain "tuned" Fe trace content, may not possess the requisite mechanical strength (*e.g.* for stent applications), and would need to be alloyed with other elements. There may, in turn, be some interplay of these additional alloying elements with Fe, which could either mitigate (*e.g.* Zr, Al–Mn) or enhance (*e.g.* Si) the influence of Fe on corrosion rate. As a result, there are probably more straightforward methods of limiting corrosion rates, such as the use of an appropriate biocompatible surface treatment or coating.

Stuart Lyon remarked: Should we be much more concerned with the influence of "low" or trace concentrations of elements in alloys and their influence on the surface structure/chemistry and corrosion?

John Scully replied: As mentioned in the closing lecture,[1] I believe that trace and minor alloying element effects are both one of the great triumphs of the corrosion metallurgy field and one of its least well understood aspects.

Consider the effects of Mo and nitrogen on stainless steels as well as Mo and W on Ni–Cr alloys. Consider minor and trace elements effects on corrosion in copper base alloys. Consider the effects of Cu and Ni or others in weathering steels. In the case of amorphous alloys, minor alloying additions are often made to improve quench rate and glass formation but effects on corrosion are not well understood. The need for understanding intensifies further in high entropy alloys.

These effects are not well understood yet provide some of the most productive area of technological accomplishments in corrosion metallurgy. Therefore, I see some of these topics as very worthy for investigation as corrosion science looks towards the future.

1 John R. Scully, *Faraday Discuss.*, 2015, DOI:10.1039/c5fd00075k.

Roger Newman responded: For the arsenic effect on dezincification, its possible analogs, and for the startling detrimental effects of elements like N and P on SCC of austenitic stainless steels (Tsujikawa), yes! By the way, the latter work is still little-known outside Japan. For pitting, and stability of passivity generally, probably not, at those very low levels. An exception is the "anodic segregation" of sulfur studied by Marcus, where the S concentration rises to monolayer levels at the metal-film interface during passivation in acid. He also proposed that similar segregation of N, in stainless steels containing that element, was responsible for resistance to pitting – I would differ on that point, having shown that N markedly reduces the dissolution kinetics in pit-like environments.

Weathering steels are another topic. Those levels are not really "trace" though. In the magnesium world, because everything else "anodically segregates", this is an important topic.

David Shoesmith responded: Yes we should. Their influence is particularly noticeable in the light metal alloys (Mg, Al, Ti) as clearly noted in the introductory address by Frankel[1] and the presentations on Mg alloys. The possible influence of Fe impurities on the anodic formation of hydrogen is not the only example of an "extreme" effect of apparently atomically-distributed impurities. The propagation of crevice corrosion on titanium alloys varies considerably as the minor content of Fe varies.

1 G. S. Frankel, S. Fajardo and B. M. Lynch, *Faraday Discuss.*, 2015, DOI:10.1039/c5fd00066a.

Simon Gibbon communicated: Listening to the discussion today I could believe that there is a real disconnect between the need to do highly defined empirical work and the need to solve less well defined real alloy corrosion problems – there is little connection to modelling. Is this really the state of corrosion science today?

James Sullivan communicated in reply: I would agree that there is probably quite a disconnect between the two and as discussed by Prof. Scully in his Concluding remarks,[1] there needs to be a collective effort by the community to bring these areas closer together in the future. This may enable us to solve and critically predict some of the complex corrosion behaviours of new and current alloys.

1 John R. Scully, *Faraday Discuss.*, 2015, DOI:10.1039/c5fd00075k.

Simon Gibbon communicated: High throughput experimentation and the access to the ability to make a wider range of alloy compositions than could ever be achieved manually, gives an incredible advantage in the search for sweet spots of corrosion resistance, but it is not fundamentally different from Edison's experiments to optimise the light bulb filament, only faster. Surely I must be missing some good examples where modelling has made/is making an explicit quantifiable contribution to overcoming significant corrosion issues?

John Scully communicated in reply: I think that high throughput experiments with higher fidelity data acquisition are certainly an opportunity to advance corrosion technology. However, I agree with the notion of "sweet spots" in many corrosion phenomena which means that a more targeted approach is required where experiments are clustered around potential sweet spots instead of massive testing of a wide range of alloy or coating compositions, for instance. As we all know, the corrosion field is full of examples where strong "thresholds" are seen. The challenge is to find and understand them.

One of the advantages of computational modeling is the ability, if the essence of the corrosion phenomenon is captured in the model, to exercise the model over many conditions to develop a better understanding of what factors really matter. Then these factors can be focused upon in more limited and focused experiments. This is different than the view you express above and in my opinion is not Edisonian.

Regarding ICCME (Computational Corrosion Materials Eng), the success stories are limited and in isolation but include tunable Al-TM-RE glass and nanocrystalline coatings that our group invented,[1–4] ultra high strength stainless steels that do not require heavy metal coatings (Questek), and iron based BMG which, maybe by accident, combine all the tools in the MSE tool box to make very corrosion resistant materials (significant Cr and Mo in solid solution, beneficial minor alloying elements such as C, B, Y, lack of inclusions or large defects *etc.*). Another example might be grain boundary engineering of polycrystalline alloys for SCC resistance. These examples stand in isolation and do not yet signal a broad movement.

1 N. R. Tailleart, B. Gauthier, S. Eidelman and J. R. Scully, Metallurgical and physical factors controlling the multi-functional corrosion properties of pulsed thermal-sprayed Al–Co–Ce coatings, *Corrosion*, 2012, **68**(3), 035006-1–035006-26.
2 J. R. Scully, F. Presuel-Moreno, M. Goldman, R. G. Kelly and N. Tailleart, User-selectable barrier, sacrificial anode, and active corrosion inhibiting properties of Al–Co–Ce alloys for coating applications, *Corrosion*, 2008, **64**(3), 210–229.
3 M. A. Jakab and J. R. Scully, On-demand release of corrosion-inhibiting ions from amorphous Al–Co–Ce Alloys, *Nat. Mater.*, 2005, **4**(9), 667–670.
4 F. Presuel-Moreno, M. A. Jakab, N. Tailleart, M. Goldman and J. R. Scully, Corrosion-resistant metallic coatings, *Mater. Today*, 2008, **11**(10), 14–23.

Janine Mauzeroll communicated in reply: On the atomic scale, *ab initio* and DFT based models have been used to understand already known corrosion inhibition, but also to predict the effect of doping. For example, models were used to study the effect of chloride ions on passive NiO films,[1] the bonding of benzotriazole corrosion inhibitor on copper and copper oxide surfaces[2] and the effect of different doping elements on the thermodynamic corrosion properties of Ni based alloys.[3] The earlier has inspired much more research and interaction between modeling and experiments on passive films and their decomposition.[4] Increasing scale size to microscopic phases in alloys and their coupling, models are still being developed. One often cited work in this field is by Kiran Deshpande[5] on the Microgalvanic coupling of alpha and beta phase in AZ91 magnesium alloys.

Most direct impact has finite element modeling of macro galvanic corrosion. Frequently used in engineering applications to estimate the effect of galvanic coupling are numerical models based on the ionic conductivity of the electrolyte, *i.e.* the Laplace equation of the electric field.[6–8]

1 Asmae Bouzoubaa, Boubakar Diawara, Vincent Maurice, Christian Minot and Philippe Marcus, *Corros. Sci.*, 2009, **51**, 2174–2182.
2 Anton Kokalj, *Faraday Discuss.*, 2015, DOI:10.1039/c4fd00257a.
3 Bai-Lin Lü, Guo-Qing Chen, Wen-Long Zhou, Hui Su and Rui Liu, *J. Nucl. Mater.*, 2011, 286–291.
4 Toni Massoud, Vincent Maurice, Lorena H. Klein and Philippe Marcus, *J. Electrochem. Soc.*, 2012, **160**, C232–238.
5 Kiran B. Deshpande, *Electrochim. Acta*, 2011, **56**, 1737–1745.
6 Nicolas Murera, Roland Oltra, Bruno Vuillemin and Olivier Néel, *Corros. Sci.*, **52**, 130–139.
7 Dao Trinh, Philippe Dauphin Ducharme, Ushula Mengesha Tefashe, Joseph R. Kish and Janine Mauzeroll, *Anal. Chem.*, 2012, **84**, 9899–9906.
8 Daniel Höche, *J. Electrochem. Soc.*, 2015, **162**, C1–C11.

Christopher Taylor opened a general discussion of the paper by Geraint Williams: As I understand your interpretation of the Mg corrosion, at higher concentrations of NaCl, you expect that the solution can support a higher throwing power, and so the radial growth of the corrosion front occurs, whereas in lower concentrations of NaCl, the throwing power is lower, thus only 1-D spreading of corrosion occurs, giving this filiform appearance. Is this process amenable to modeling? It is not clear to me how changing the throwing paper should lead to a shift in geometry, only in rate, so I would find a mathematical model convincing. Can you describe how the geometry of the corrosion front changes in the intermediate case, as one moves from higher concentration (radial) to lower concentration (1D)?

Geraint Williams responded: I would be more than happy to see the phenomenon modelled and willing to supply the relevant experimental data to any volunteer who felt like taking on such an endeavour. For the intermediate case (between 0.1 M and 0.01 M NaCl), the breakdown of the Mg surface causes initial propagation of circular features, but as they grow radially, the anodic region at their perimeters starts to fragment. Consequently, filiform-like tracks emanate from these points of fragmentation, as shown in the photograph (see Fig. 1) of a post-corrosion Mg surface after immersion in 0.02 M NaCl (aq), and disc-like corrosion propagation stops.

Alison Davenport asked: The growth velocity of the corrosion filaments can be converted into a current density. Could you comment on the range of current density values found, and in particular if there is a minimum current density below which filament growth cannot take place?

Geraint Williams answered: Yes it is correct that velocity can be converted to a current density value, although this requires some assumptions to be made regarding the depth of anodic dissolution and the width of individual filaments. In a previous paper,[1] a more rigorous characterisation of filiform corrosion affecting the same type of Mg under similar chloride ion concentrations was described. In this work the minimum filament width observed was 0.1 mm and a depth of attack of *ca.* 1 μm was estimated by AFM mapping. Using an average filament velocity of 1 μm s^{-1} and assuming the front of the "track" comprises a 3 dimensional rectangle of width 0.1 mm, length 10^{-3} mm and depth 10^{-3} mm,

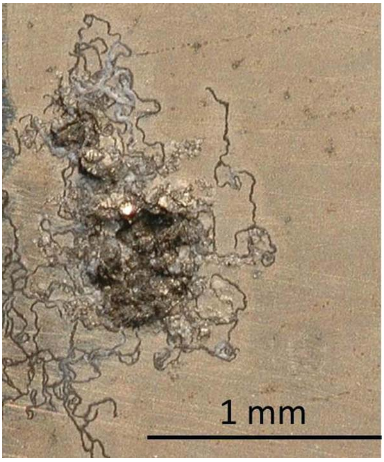

Fig. 1 Photograph of a post-corrosion Mg surface after immersion in 0.02 M NaCl (aq).

then it can be calculated that a mass of Mg equating to 1.8×10^{-10} g is excavated every second (using density (Mg) = 1.8 g cm^{-3}). Using Faraday's law this works out as a current of 1.4 μA and if it is further assumed that the area from which it emerges comprises the rectangle face (width 0.1 mm, length 10^{-3} mm), then the current density becomes 14 A m^{-2}. Given that filament velocity values never fall below 0.7–0.8 μm s^{-1} and that the minimum width is *ca.* 0.1 mm, then it appears that current density values of at least 10 A m^{-2} are required to sustain propagation. This correlates well with SVET-derived anode current density values of between +5 and +15 A m^{-2} reported in the aforementioned publication.

1 G. Williams and R. Grace, *Electrochim. Acta*, 2011, **56** 1894.

Gerald Frankel asked: It seems that you should be able to understand the phenomenon by assessing the cathodic activation after corrosion using polarization curves. This might vary with the chloride concentration similar to the effect of the prior applied anodic current density. In that case, the corrosion morphology might be controlled by the amount of available cathodic current and galvanic coupling rather than by the ohmic resistance.

Geraint Williams responded: Yes, this is certainly a possibility that should be considered. However, there will be some difficulty in reproducibly generating a working electrode area which is fully corroded, especially where filiform attack is prevalent and there will be some "islands" of uncorroded surface remaining amongst the network of dark tracks, even after protracted immersion. Also, there may be some issues in effectively accounting for *iR* drops in carrying out potentiodynamic experiments on fully corroded surfaces over a range of different chloride concentrations, even in the presence of a Luggin capillary. One would also have to think of a physical description of why chloride ion concentration would influence the electrocatalytic efficiency of the corroded surface toward cathodic hydrogen evolution.

David Shoesmith asked: You elegantly demonstrate the relationship between anodes and cathodes and show how corrosion tracks across the surface. Is the substrate microstructure at all involved in determining the direction of propagation?

Geraint Williams responded: There is no real indication, especially at concentrations of 0.1 M NaCl (aq) and above, that propagation is influenced by microstructure for the pure Mg studied here. There are reports in the literature,[1] that indicate filiform corrosion (FFC) on pure Mg can preferentially follow certain crystallographic features of the Mg grains. These authors showed that directionality of individual filaments appeared to be influenced by changes in orientation at grain and twin boundaries. However, the investigation was carried out in chromate inhibited dilute chloride electrolyte, which is not the case for the present work disseminated in this Faraday discussion. The random walk FFC patterns observed upon immersion in 0.01 M electrolyte (see Fig. 1c), for the rather impure form of Mg studied in our work, suggests that microstructural influence on filament directionality is minimal in the absence of dissolved chromate inhibitor.

1 P. Schmutz, V. Guillaumin, R. S. Lillard, J. A. Lillard and G. S. Frankel, *J. Electrochem. Soc.*, 2003, **150**, B99.

Clara Wren opened a general discussion of the paper by Janine Mauzeroll: Your sensors use microcapillaries for local corrosion potential measurements. Mg corrodes very fast and, as far as I can tell, this corrosion is often limited by the solution transport rate. Do you expect the same solution transport behaviour for redox species in the microcapillaries and in bulk water? How do you ensure that what you are measuring is not the transport limited corrosion potential inside the microcapillary?

Janine Mauzeroll answered: The question is referring to the measurement of corrosion potential of the different microstructures using the microcapillary technique presented in Figure 1 of our paper. For this measurement, the meniscus of the filled micropipette is brought in electrical contact with the substrate where the open circuit potential is recorded. This experiment does not consist of any measurement of substrate kinetics and we do not extract any rate information where solution transport is important, as previously mentioned.[1] When performing a substrate polarization curve, we assume that the mass transport within the micropipette will be governed by diffusion only within the confines of the micropipette. The comparison of numerical simulations for mass transport governed by diffusion only within micropipettes (~500 nm) is in excellent agreement with experimental data.[2]

1 S. Thomas and H. Bohni, Analytical Methods in Corrosion Science and Engineering. CRC Press, Boca Raton, FL, USA, 2005, pp. 649–696.
2 Williams *et al., Anal. Chem.*, 2009, **81**, 2486–2495.

David Williams remarked: The shear force-controlled scanning vibrating capillary seems a very powerful general tool to me, analogous to the SNOM. I wonder what other probe methods you have considered that might utilise this platform – for example scanning ion conductance microscopy to map solution conductivity changes or using the capillary as a waveguide to implement optical microscopy or perhaps Raman. I wonder also if the modulation of the signal caused by the vibration could be used to advantage.

Janine Mauzeroll answered: The shear force controlled scanning vibrating capillary can be adapted for many situations in corrosion science simply by changing the nature of the probe.

In its unmodified state, the scanning droplet cell remains versatile towards electrochemical techniques that can be performed locally such as potentiodynamic polarization or voltammetry to extract local kinetics through accurate corrosion modeling. The wide variety of electrochemical techniques also include, local chronoamperometry that can probe ions released during the corrosion process[1,2] or even perform local modification of surfaces.[3,4]

It can be easily adapted to measure local impedances, making it very useful in the study of ageing and failure of protective coatings.[5–8]

It can be adapted to quantify several chemical fluxes generated during the corrosion. For example, corrosion product deposition affects the SECM feedback regeneration of different dissolved redox mediators such as FcMeOH when an alloy is immersed in a corroding solution.[9] It can also be used to directly track hydrogen fluxes from the alloy microstructure.[10] It can also be modified through the use of an ion-selective microelectrode to track Mg^{2+} fluxes.[11] Finally, with minor microelectrode manipulations, it is possible to pull fiber optics and to monitor combined spectroscopy and electrochemistry as reported by A. J. Bard in the early 2000s.[12] I cannot conclusively comment on if the modulation of the signal caused by the vibration could be used to advantage.

1 K. A. Lill, A. W. Hassel, G. Frommeyer and M. Stratmann, *Electrochim. Acta*, 2005, **51**, 978–983
2 M. M. Mennucci, M. Sanchez-Moreno, I. V. Aoki, M. C. Bernard, H. G. Melo, S. Joiret, and V. Vivier, *J. Solid State Electrochem.*, 2012, **16**, 109–116.
3 M. M. Lohrengel, A. Moehring and M. Pilaski, *Fresenius' J. Anal. Chem.*, 2000, **367**, 334–339.
4 M. Pilaski and M. M. Lohrengel, *Electrochim. Acta*, 2003, **48**, 1309–1313.
5 F. Zou and D. Thierry, *Electrochim. Acta*, 1997, **42**, 3293–3301.
6 D. Snihirova, L. Liphardt, G. Grundmeier and F. Montemor, *J. Solid State Electrochem.*, 2013, **17**, 2183–2192.
7 A. M. Mierisch and S. R. Taylor, *J. Electrochem. Soc.*, 2003, **150**, B303–B308.
8 M. W. Wittmann, R. B.Leggat, S. R. Taylor, *J. Electrochem. Soc.*, 1999, **146**, 4071–4075.
9 W. Liu, F. Cao, Y. Xia, L. Chang and J. Zhang, *Electrochim. Acta*, 2014, **132**, 377–388.
10 U. M.Tefashe, M. E. Snowden, P. Dauphin-Ducharme, M. Danaie, G. A. Botton and J. Mauzeroll, *J. Electroanal. Chem.*, 2014, **720–721**, 121–127.
11 P Dauphin Ducharme, R. M. Asmussen, D. W. Shoesmith and J. Mauzeroll, *In situ* Mg^{2+} release monitored during magnesium alloy corrosion, *J. Electroanal. Chem.*, 2015, **736**, 61–68.
12 Y. Lee, S. Amemiya and A. J. Bard, Scanning electrochemical microscopy. 41. Theory and characterization of ring electrodes, *Anal. Chem.*, 2001, **73**, 2261–2267.

Stuart Lyon opened a general discussion of the paper by Sannakaisa Virtanen: Given the low net atomic number of Mg-based implant alloys, how can they be easily imaged by X-rays?

Sannakaisa Virtanen answered: They cannot be easily imaged by X-rays. So I assume one would try to use some X-ray markers. In the case of coated Mg-based implants, the coating could provide also a means for imaging. I am not aware if there is a state-of-the-art in the field, or simply some exploratory approach.

Rob Lindsay said: From reading your paper, I believe you have assumed a homogenous substrate for quantification of the XPS data. Clearly, if this is true, this substrate model does not represent reality particularly well, in my opinion, as there will be discrete layers of material, with the metallic substrates lower most. How do think your approach impacts upon your interpretation of the XPS data (*e.g.* data shown in Fig. 8)?

Sannakaisa Virtanen replied: The XPS data presented simply shows the at% determined, and is not further interpreted for instance in view of a homogeneous or partial coverage or in view of the different layers from the metallic substrate, to passive film, to the protein adsorption layer. We do not believe that we have a well-ordered and complete monolayer of albumin in this case. The XPS data should be considered only in a qualitative manner, *i.e.* in comparison of the different systems (substrate material, time, electrolyte). In order to perform a full analysis, more experimental data would be required, including information on coverage and thickness of the different layers.

Kirsi Yliniemi remarked: In addition to the nature of surface charges on either Mg or Fe surfaces, could you comment how the surface charge density affects the protein adsorption as it may also influence your results? There exist models which suggest that at low surface charge densities polyelectrolytes adsorb on a more flat orientation (2D films) while at higher surface charge densities thicker 3D film starts to grow (see for example the review[1]).

[1] A. Dobrynin and M. Rubinstein, *Prog. Polym. Sci.*, 2005, **30** 1049–1118.

Sannakaisa Virtanen replied: Thank you very much for the important comment and helpful literature. Yes, indeed not only the type of surface charge but also the charge density should play a role. Until now, we did not carry out any detailed studies on this, and the surface charge considerations in our paper are simply based on IEP values found in the literature.

But indeed we would like to know more about the type of the protein adsorption layers, so in addition to addressing the question on the amount of protein adsorbed on different surfaces, we would like to study the orientation of the proteins on the surface (with additional experiments and a more detailed data analysis) and also their functionality (for instance, are they in their native conformation or possibly denaturated, depending on the surface they are adsorbing on).

In the case of Mg some of the studies we would like to do are challenged by the high reactivity of the Mg surfaces in aqueous solutions, so we often have the problem of not only adsorption of proteins taking place but at the same time substantial corrosion of the substrate (this is also briefly mentioned in the paper).

Johannes Lützenkirchen communicated: I have a comment concerning the remark in the introduction of the paper, where you mention that from your references 14, and 19–27, “both acceleration and inhibition of corrosion has been observed" with respect to the action of proteins related to Mg-materials. Your interpretation is based on the charging of the adsorbing surface and that of dissolved protein. The opposite sign of charge should favor adsorption and cause inhibition. In that respect you quoted from your reference 38 a compilation of points of zero charge for Mg-related surfaces. Indeed the points of charge of particles of these materials have been reported to be high (*i.e.* above pH 10), but a scan of references 14, and 19–27 of your paper shows that usually flat surfaces have been used in the adsorption and corrosion studies. It has been previously observed that such flat surfaces may have points of zero charge that are much lower than those of the corresponding particles.[1–4] It is one issue we discuss in our paper. Fig. 2 shows unpublished zeta-potential measurements for a flat MgO surface in 5 mM NaCl. The system has been titrated under purified and humified Argon atmosphere, using HCl and NaOH solutions. We used freshly prepared NaOH solution to exclude carbon dioxide. The MgO surface is expected to hydroxylate and expose a $Mg(OH)_2$ like surface to the solution. Even for this "MgO"-surface, we retrieve a drastic difference between particles and flat plates. It has been shown that this feature also occurs on alumina specimens of different orientation,[2,3] so that it is not related to the surface chemistry.

The isoelectric point (IEP) of the sample was initially at pH 4 as shown in Fig. 2. On aging the IEP increases, but remains below pH 5 (data not shown), *i.e.* still much lower than the powder values from ref. 38 of our paper. It is important to note that data on sapphire-c surfaces show that roughness decreases the IEP of this plane to even lower values (Lützenkirchen *et al.*, manuscript in preparation).

Furthermore, the wide variation of the IEPs in Kosmulski's collection (ref. 38) of many samples would make conclusions based on literature data alone arbitrary for many cases. Thus the use of published particle IEPs does not necessarily give an appropriate interpretation. Even for nominally identical solids, the IEP may vary widely. Therefore, it is favorable to measure it for the conditions used. In particular since adsorption of some proteins may occur even under electrostatically unfavorable conditions.[5] Although in the present case, no contradiction occurs between the charge-interpretation and the experimental data, in general the point of zero charge of a given sample should be determined to avoid ambiguity.

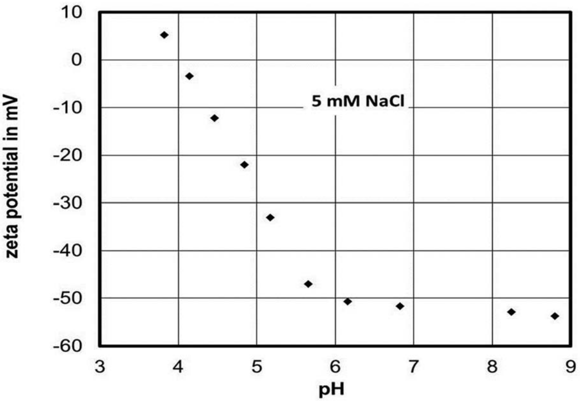

Fig. 2 Zeta-potential of a flat MgO surface in 5 mM NaCl.

A related question concerns the iron samples. Does the entry in Table 2 invoke that ferrous iron is the relevant form of iron? The background of the question is that, while ferric oxides, hydroxides and oxyhydroxides are easily studied and the IEPs can usually be determined quite well, iron(II) oxide and hydroxide minerals are much more difficult to investigate. One major difficulty is that it is crucial to avoid oxidation of iron(II). Very few studies on these iron(II) systems are therefore available and only recently it has been reported[6] that the IEPs of most of the iron(II) samples under investigation in that study exhibited IEPs of about 10 or higher.[6] The substrates also showed transformation phenomena. The data from ref. 38 (in your paper) are all for pure iron(III) systems or magnetite. How would the interpretation be affected if you considered the higher IEPs from the recent study?[6]

1 G. V. Franks and Y. Gan, *J. Am. Ceramic Soc.*, 2007, **90**, 3373–3388.
2 G. V. Franks and L. Meagher, *Colloid Surf. A-Physicochem. Eng. Asp.*, 2003, **214**, 99–110.
3 J. P. Fitts, X. Shang, G. W. Flynn, T. F. Heinz and K. B. Eisenthal, *J. Phys. Chem. B*, 2005, **109**, 7981–7986.
4 E. Mączka, J. Luetzenkirchen and M. Kosmulski, *J. Colloid Interface Sci.*, 2013, **393**, 228–233.
5 T. Arai and W. Norde, *Colloids Surf.*, 1990, **51**, 1–15.
6 E. Maczka, E. Jartych and M. Kosmulski, *Colloid Surf. A-Physicochem. Eng. Asp.*, 2014, **441**, 326–330.

Sannakaisa Virtanen communicated in reply: Thank you for the very interesting comments and questions and also for sharing some unpublished data. I completely agree that our approach is a rough and simple one, as certainly the IEP values should be measured for the sample surfaces under the conditions of the study, to have a better and more realistic view. Also, I agree that surface charge is not the only factor influencing protein adsorption, for instance surface wettability is also of importance. If other driving forces are stronger than electrostatic interactions, then adsorption could take place as you mention also for electrostatically unfavorable conditions. In our case, as both Fe and Mg surface are hydrated and show a similar hydrophilic behaviour, according to the literature electrostatic interactions can be more significant.

As regards the nature of the Fe surface: The passive film formed in NaOH should be an oxide with a mixed valency between Fe_3O_4 and Fe_2O_3 (but not FeO). We refer to the values for $FeO/Fe(OH)_2$ in Table 2, as we assume a hydroxide deposit layer on top of the Fe-oxide layer. Again, a determination of IEP values for the given case should be carried out.

The discussion in the manuscript is based on the fact that our hypothesis on the relevance of the surface charge argument seems to hold for two different proteins. But it still remains a hypothesis.

Clara Wren opened a general discussion of the paper by James Sullivan: Your corrosion rate decreases with the aluminium content in the alloy. Have you tried to normalise the corrosion rate with respect to the same zinc–magnesium or magnesium content? Is the change in corrosion rate simply a function of the relative amount of magnesium available, or is there any synergistic effect of the composition-induced alloy-microstructure on the corrosion rate?

James Sullivan replied: We haven't tried to normalise the data to date but that is an interesting suggestion. I think the ultimate change in corrosion rate of these alloys is dependent on both alloy additions (Mg and Al) especially in atmospheric corrosion conditions where the establishment of Al and Mg corrosion products are critical for the performance of these alloys. I feel the initial corrosion rate differences observed here maybe more dependent on increasing Al levels with a greater coverage of alumina present as the eutectic volume fraction increases that is more resistant to corrosion initiation in the earliest of stages.

Stuart Lyon asked: What is the specific composition of the various components of the eutectic in these complex Zn–Al–Mg alloys? How does the area/volume fraction of eutectic influence the overall corrosion performance?

James Sullivan answered: We haven't performed a detailed experimental analysis of the various phase compositions. MTDATA simulations were performed for ZMA 2 during its development that suggested that the binary eutectic contained $MgZn_2$ and Zn lamellae with around 1% Al in the Zn lamellae and 0.6–0.8% Al in the $MgZn_2$. In the ternary eutectic the same phases were present with addition of an Al fcc phase containing 66% Al, 0.02% Mg and the remainder Zn. The volume fraction of eutectic and its influence on corrosion performance are given in the presented paper in Figures 3 and 7 and show a fairly linear relationship between increased corrosion performance with increasing eutectic volume fraction.

Gerald Frankel said: Why doesn't the attack in the eutectic region go deep into the structure and why does it initiate at only a few places and then spread across the surface?

James Sullivan responded: The attack does also penetrate vertically into the sample and we have seen this from examination of cut samples post corrosion although it would seem that the rate of lateral spreading is greater. The reason for the corrosion spreading through the eutectic laterally at the surface may be due to the surface being more eutectic rich as the solidification sequence starts with nucleation of Zn rich dendrites at the steel substrate. Therefore the volume fraction of primary Zn is greater at the coating/steel interface with a subsequent reduction of primary Zn and increase in eutectic as the coating is traversed to the surface. As the $MgZn_2$ in the eutectic is the preferential phase for initial corrosion attack then lateral attack through this eutectic rich surface may dominate.

Arjan Mol asked: First, I would like to thank James Sullivan for presenting this very interesting work and paper during this Faraday Discussions session, I greatly enjoyed it. My question is the following: can you please show, explain and/or comment on the positions and evolution of (local) cathodic and anodic areas in the SVET measurements with time and their correspondence to those in the time-lapse optical microscopy videos considering a.o. the different lateral resolutions of the techniques?

James Sullivan responded: That is an interesting question. The SVET samples are much larger, 10 × 10 mm compared with the 1mm diameter circle area of the time lapse samples. The SVET has a practical resolution of around 150 microns. On the SVET maps we see localised anodes that are well spaced apart (>1 mm) and have a radius of approximately 500 microns. It must be remembered that this reflects the current flux from the anodic features that the SVET detects in its plane of scan 100 microns above the sample surface. As the SVET scans progress the anodic features actually spread out as small rings from the initiation point. I have attached a movie to show this.† It is somewhat difficult to correlate this with the time-lapse movies due to the differences in sample area and resolution of the techniques but the spreading of the anodes as rings may reflect the lateral growth of the anodic features shown in the time-lapse videos. Obviously, the growth of features in the time-lapse experiments maybe more constrained due to the smaller sample area exposed.

Steven Street asked: The three different ZMA alloys had quite different dendrite sizes, indicating different thermal gradients when solidifying. As corrosion seemed to propagate in the interdendritic regions, is there any value in trying to refine the size of these dendrites? Would this improve the corrosion behaviour of these alloys?

James Sullivan responded: These experiments at a range of cooling rates were carried out using a 1.6 wt% Mg 1.6 wt% Al ZMA alloy during the development phase of this alloy and little difference was observed during industrial corrosion tests. It would be interesting to see if any effects of morphology could be identified using this technique. Within the group we have certainly seen that morphological differences within the microstructure induced by cooling rate changes seem to influence the corrosion behaviour of Zn - 4.8 wt% Al alloys.[1]

[1] J. Elvins, J. A. Spittle and D. A. Worsley, *Corros. Eng.*, *Sci. Technol.*, 2003, 197–204.

Stuart Lyon asked: Corrosion resistant metallic coatings on steel are much thinner than they used to be. How does this influence the corrosion process/resistance at the cut edge?

James Sullivan answered: These ZMA coatings are certainly thinner than more traditional HDG type coatings but in industrial salt spray tests they certainly outperform the HDG materials during surface testing. We also see this improvement in corrosion performance when examining surface corrosion. At the cut edge we have comparable performance to that of HDG for the thinner ZMA coating in SVET and external run-off testing that is encouraging considering the change in anode/cathode ratio. However, the performance at the cut edge is not nearly as improved as the surface performance in comparison to HDG, that may reflect this change in anode/cathode ratio.

Clara Wren remarked: What is the geometry of the viewing cell, the diameter and the depth of the solution, with respect to that of the rest of the corrosion cell? I noticed in your video images that the corrosion front always starts close to the boundary between the viewing area and the rest of the corrosion cell. Could your observation indicate that the Mg corrosion is solution transport limited?

James Sullivan answered: The distance between the viewing window and the sample is around 1 mm so there is a 1 mm body of electrolyte between the sample and the window. The diameter of the protective shroud on the microscope is 20 mm. The total volume of electrolyte in the cell is 250 ml and electrolyte is accessible to the sample from 360° from the bulk volume into the 1 mm gap as shown in Figure 1 in the paper. The corrosion often starts near the periphery of the exposed area as the circular area is masked using Teflon tape. The slight geometry change near the tape is often sufficient to induce anodic activity here and we also see this fairly regularly in SVET experiments where again a sample area is masked off using tape. We plan to carry out some tests involving stirring to assess the effect on the corrosion mechanism and to assess if diffusion of species is restricted into the gap above the sample but I feel with a 1 mm gap there maybe sufficient space for electrolyte diffusion especially as it can access the sample from the full circumference around the shroud.

David Williams commented: I'm interested in the patterns and timing of appearance of the dark shadows that correspond to precipitation of the corrosion products – for example the sudden appearance of a ring that fades and then reappears. There seems to be some rich information here about the development of the anodic and cathodic sites and convection–diffusion–reaction in the immediate vicinity of the interface. Are you able to comment on this?

James Sullivan replied: I too feel that this is potentially showing some interesting information about the nature of anodic and cathodic sites, the ionic diffusion between the two electrodes and pH gradients established between them. The pH effects have been demonstrated in some previous work[1] using a phenolphthalein indicator and is visible due to the dissolution of Mg corrosion products as the front of anodic activity moves, presumably as the pH drops local to the anodic site. I think it may also be interesting to see the effect of electrolyte concentration on the formation of the corrosion product rings with regards to the distance from the anode to assess the effect of the electrolyte's throwing power on anode-cathode spacing.

1 James Sullivan, Shahin Mehraban and Jon Elvins, *Corros. Sci.*, 2011, **53**(6), 2208–2215.

Su-Ting Cheng said: In Fig. 2, the red area increases largely from ZMA1 to ZMA3. Since the bulk concentrations of Zn (green) and Mg (red) are kept the same, a different colour distribution could indicate a surface segregation of Mg. Have you ever measured the concentration of elements throughout the whole depth of the specimens? We have studied the Mg–Zn system with DFT, and the results tell us the surface of the $MgZn_2$ intermetallic compound is more stable with a higher surface Mg concentration, either in vacuum or in contact with oxygen. It would be nice to see if this could be also observed in experiments.

James Sullivan responded: I may have misunderstood the question but the quantity of Mg increases from 1–3 wt% from ZMA 1–3 and the Zn level drops as the Mg and Al levels increase. This I believe accounts for the increase in red as the volume fraction of eutectic increases in the microstructure from ZMA 1–3. At present we have not measured the depth profile of the elements.

Rob Lindsay stated: I was wondering if you believe that the filamentous precipitates you observe (as shown in Fig. 10 (B)) are important for controlling corrosion or are just an interesting phenomenon?

James Sullivan replied: The filaments are an interesting phenomenon but I think they can offer an important role in controlling corrosion as the deposition of the filaments occludes the surface from further attack potentially. I think the initial stages of precipitation local to the anodic features also demonstrates quite nicely the formation of inhibitor films at the anode. Also, these conditions may reflect those occurring in drying electrolyte films where concentration of salts may become saturated.

Simon Gibbon commented: Yesterday Mira Todorova[1] told us about the application of point defect models to give new insights into the defects formed on zinc surface which could lead to corrosion. In your paper you have considered the corrosion behaviour of commercially important zinc alloys. I would be interested to know if you have considered applying such models to help in the understanding of your systems?

[1] Mira Todorova and Jörg Neugebauer, *Faraday Discuss.*, 2015, DOI:10.1039c/4fd00238e.

James Sullivan answered: This is not something we have considered to date but it would be of interest to assess how the model could be applied to these alloys to provide a prediction of corrosion behaviour with regards to preferential attack.

Trevor Hughes communicated: A very interesting paper on the use of *in situ* time-lapse optical microscopy to compare the corrosion behaviour of Zn–Mg–Al alloys in 1% NaCl at pH 7. In the paper it is stated “it may be counterintuitive that an increased eutectic volume would reduce the corrosion rate given that these phases are preferentially attacked in the microstructure but it would seem that increased levels of Mg and Al in the alloy create more robust oxide layers due to their rapidity of reaction and the passive nature of Al_2O_3.” Question 1: Have the authors looked at brines with different pH, presumably the passive oxide layers would not be stable in alkaline (pH 10–11) brines? What are the pH limits of such passive oxide layers. In addition, for the neutral (pH 7) system, what is the effect of elevated temperatures?

The paper also shows that the corrosion rate of the ZMA2 alloy (1% NaCl, pH 7) decreases in the presence of sodium phosphate (0.0001, 0.01 mol L^{-1} Figure 13). Question 2: How does this response to phosphate compare for the 3 alloys studied and for pure Zn?

James Sullivan communicated in reply: We are currently undertaking a matrix of tests that include varying the pH with pH levels of 3, 7 and 10 coming under examination. To date I cannot give a detailed report on the results as they are fairly preliminary but the initial indications do indeed show visual differences to the progression of corrosion and formation of corrosion products. We have not carried out any tests as of yet at an elevated temperature and to date we have only carried out the Phosphate tests on ZMA2. However, a pure Zn test is in the matrix of tests planned.