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DISCUSSIONS

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Reactions at the nanoscale: general discussion

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Richard Nichols opened a general discussion of the paper by Olaf Magnussen: You state that perchlorate is not absorbed on bismuth. What is the evidence for this? For example is this apparent from the voltammetry?

Olaf Magnussen answered: Previous studies of Bi UPD on Au(111) and Au(100) have observed identical adlayer structures in perchloric and sulfuric acid solution and concluded that both anions are not specifically adsorbed or at least have no decisive influence on the UPD structure. For this reason, also no major anion influence is expected at the more negative potentials of the bulk deposition regime.

Wolfgang Schmickler asked: The bismuth ion is triply charged; it must have an energy of solvation of about 50 eV. So it is extremely difficult to shed this solvation sphere. How is this ion deposited? Does it form a complex with anions?

Olaf Magnussen replied: The chemistry of Bi complexes in aqueous solution is very rich. However, in the strongly acidic solution used in our experiments simple aquo complexes of Bi^{3+} with (six) water ligands should be the predominant species. RDE measurements of the charge transfer kinetics[1] report a stepwise charge transfer, but details on the ion transfer process are not understood to my knowledge.

[1] I. Valsiūnas, L. Gudavičiūtė, V. Kapočius and A. Steponavičius, *Chemija*, 2006, **17**, 11.

Patrick Unwin asked: Are you able to determine kinetics from measurements at the nanoscale and do these scale up and relate to macroscopic measurements? Do you have a feeling for how big the inhibition of mass transport by the tip is?

Olaf Magnussen answered: The inhibition of Bi deposition is significant, approximately one to two orders of magnitude. For this reason we did not analyse the Bi growth rates quantitatively. However, for the quantitative analysis of the probability of a kink to be in one of the three different states this does not pose a problem, because the mass transport required for the latter is negligible (a change from a type B to a type A or a type C kink only requires addition of a single atom).

Marc Koper inquired: Can you say anything from the images about the nucleation of these structures?

Olaf Magnussen replied: As mentioned in the paper, nucleation of the Bi nanochains on Au(100) occurs predominantly at the edges of Bi islands, but can occasionally also be observed in the center of extended Bi terraces.

Kristina Tschulik asked: You occasionally observed the formation of Bi nanowires of well-defined orientation with respect to the substrate. Are these wires re-formed at the same position when you cycle the potential to sequentially dissolve and re-deposit them? If so this could hint towards a preferred nucleation of these wires at specific sites, *e.g.* point defects.

Olaf Magnussen answered: All Bi nanowires as well as the nanochains on Au(100) are epitaxial to the underlying substrate. Nucleation of these wires was indeed found to occur preferentially at surface defects, such as steps or domain boundaries in the Bi UPD layer (see also ref. 13 and 59 of the manuscript).

Zhongqun Tian remarked: You have demonstrated the power of this technique in terms of spatial and time resolution. I wonder how far can it move forward, especially regarding the sensitivity. The *in situ* monitoring of deposition growth is surely important, but for almost all practical applications in electroplating, additives are used to improve the smoothness and metal quality. Would it be possible to observe these or some additive adsorption during the deposition process?

Olaf Magnussen replied: Indeed, such insights are in principle obtainable. In previous video STM studies we have investigated the surface dynamic behaviour of anionic as well as small organic molecules, such as methyl thiolate, including the interaction of these species with Cu adatoms and steps.[1–3] However, similar studies of larger organic adsorbates are challenging at present. In this case low tunneling currents of ≤100 pA are required for STM imaging, in order to avoid significant modifications of the surface dynamics by the STM tip. In our current video STM the high bandwidth of 600 kHz effectively limits the average tunneling current to values of ≥1 nA. Lowering this value should be possible, but will require significant improvements in the design of the STM head and preamplifier.

[1] Y.-C. Yang, A. Taranovskyy and O. M. Magnussen, *Angew. Chem. Int. Ed.*, 2012, **51**, 1966.
[2] Y.-C. Yang, A. Taranovskyy and O. M. Magnussen, *Langmuir*, 2012, **48**, 14143.
[3] Y.-C. Yang and O. M. Magnussen, *J. Electroanal. Chem.*, 2014, **716**, 80.

Serge Lemay opened a general discussion of the paper by Katharina Krischer: The power spectrum for a stochastic signal consisting of uncorrelated exponentially decaying pulses has the form $S(f) = S_0/(1+(2\pi f/a)^2)$, where a is the decay constant of the exponential. This universally yields a $1/f^2$ decay in $S(f)$ at high enough frequencies; the main piece of quantitative information that can be extracted from the spectrum is the value of a, which determines the frequency below which the spectrum deviates from the inverse square law. With this in mind, it seems that the observation of a nearly $1/f^2$ spectrum in the data presented here simply reflects the shape of the individual impulses, and that the more interesting dynamics may occur on longer time scales. However, the corresponding frequency range (below 10^{-1} Hz) is not studied in the manuscript. What are the prospects for obtaining sufficiently long time traces so that these ultra-low frequencies can also be analyzed?

Katharina Krischer answered: This is a very good point. If you look carefully at the time series in the manuscript, you observe that they exhibit a slow drift. This unfortunately restricts the measuring time, and for this reason we refrained from evaluating the spectra at lower frequency in more detail. Still, we observed that the power spectra do not exhibit any preferred frequency. Hence, it is unlikely that any of the three types of noisy or spiky time series are related to an underlying oscillatory dynamics. We argue that instead the fluctuations are induced by molecular noise that is amplified to a mesoscopic or macroscopic level. In our view, this is a quite remarkable feature. However, it is also clear that further studies, in particular stochastic simulations, are necessary to understand the dynamic features of the system better.

Wolfgang Schmickler commented: The critical size of 25 μm is quite large on an atomic scale. Can it be related to any other characteristic length in your system?

Katharina Krischer replied: Yes, the characteristic domain radius depends on an interaction between the autocatalytic surface reaction and diffusion of CO in front of the electrode. From the theory of nonlinear dynamics it is known that the critical radius of a circular domain can be estimated as $\frac{D}{\sqrt{Dk}}$, where D is the diffusion constant and k is the characteristic rate constant of the autocatalytic reaction. In our case, the 'autocatalytic reaction' is really a network of reactions and is not related in a simple manner to an individual rate constant entering the model. With the given D and k of approximately 1 s^{-1}, which seems to be a realistic value, a rough estimation of the critical radius of a domain amounts to about 30 microns. Note that this is only a rough estimate, and for microelectrodes the critical size depends also on the size of the microelectrode since diffusion becomes the more effective the smaller the electrode is. This trend is captured correctly in our simulations. Note that in the ms we estimate the critical size of the nucleus from the width of the interfacial region of a planar interface between a CO covered and a bare electrode, which is proportional to $\sqrt{\frac{D}{k}}$. This gives the same estimation.

Marc Koper asked: What would happen if instead of one microelectrode you would have an array of microelectrodes? Would you see phase separation as on one macro-sized electrode? Would you expect any spatial or temporal self-organisation?

Katharina Krischer replied: This is an interesting question. When one performs a slow galvanodynamic scan with an array of microelectrodes, one electrode after the other is ignited, leading thus at intermediate current densities to a partitioning of the array into active electrodes and CO covered passive ones. One of those electrodes might also exhibit an intra-electrode phase separation as in the present example. For an intermediate, constant current density, the response might be even more complex: under some conditions, inter-electrode switching is observed, such that some electrodes exhibit more or less regular transitions from an active state to a passive state and back. Furthermore, especially at relatively high current densities, *i.e.* when nearly all electrodes are activated, a Hopf bifurcation might occur resulting in true limit cycle behavior. Note that these oscillations are only due to the global coupling of the array of bistable electrodes. Hence, there is no feedback in the reaction mechanism that causes the oscillatory behavior. In fact, before we did the present study of the intra-electrode dynamics we studied the inter-electrode dynamics of an array of four microelectrodes. Some of what I explained can be found in our publications.[1,2] Finally, I should note that all dynamics I discussed refers to an array configuration and to simulations where the global coupling through the galvanostatic mode is dominating. When the electrodes are placed closer together, diffusional coupling between the electrodes also occurs. I would speculate that the dynamics will still be dominated by the global coupling, but there are so far no experiments or simulations that support this hypothesis. Hence, it is possible that the spatio-temporal behavior becomes even more complex.

1 D. A. Crespo-Yapur, A. Bonnefont, R. Schuster, K. Krischer and E. R. Savinova, *ChemPhysChem*, 2013, **14**(6), 1117–1121.
2 D. A. Crespo-Yapur, A. Bonnefont, R. Schuster, K. Krischer and E. R. Savinova, *ChemElectroChem*, 2014, **1**(6), 1046–1056.

Marc Koper said: How do you prepare your micro-electrodes, and how do you verify their cleanliness? We find that Pt ultramicro-electrodes tend to be too contaminated to study very structure sensitive electrocatalytic reactions.[1]

1 L. Jacobse, S. J. Raaijman and M. T. M. Koper, *Phys. Chem. Chem. Phys.*, 2016, **18**, 28451–28457.

Katharina Krischer answered: The preparation of the microelectrodes is certainly the most critical point in the experiments. Therefore, let me describe it in detail. However, before doing so I would like to note that in CO electrooxidation experiments the strong adsorption of CO on the electrode surface protects the surface from other impurities such that the problem here might be somewhat less severe than with other electrocatalytic reactions. As for the preparation of the electrode: The microelectrode surface is first polished on an adhesive polishing disk (PRESI, reference: 00162160) with a mixture of diamond suspension REFLEX LDP 1μ (PRESI, reference: 00242610) and Lubricant REFLEX LUB (water based lubricant, PRESI, reference: 00242700). The polishing is done by describing a figure 8 with the microelectrode, after 10 cycles, the electrode is rotated by 90° and the procedure is repeated again until the electrode comes back to its starting position. At the end the microelectrode is rinsed under a flow of ultrapure water for 1 minute.

The same procedure is repeated with a mixture of diamond suspension REFLEX LDP 1/4μ (PRESI, reference: 00242600) and Lubricant REFLEX LUB (water based lubricant, PRESI, reference: 00242700). After rinsing with water, the electrode is put into a small beaker (10 mL) containing the electrolyte for 5 minutes, then the electrode is taken out of the beaker, rinsed with electrolyte (50 mL), and again rinsed with a flow of ultrapure water for 1 minute.

The complete set of tools (beakers, pipettes, flasks, cells, corks…) used to prepare or contain electrolyte is put once a week overnight into a mixture of 1 : 1 sulfuric acid (96% Merck) and hydrogen peroxide (32% VWR), then rinsed with water (8 times) and subsequently filled with water for 4 h and rinsed again 8 times with ultrapure water. All the material is filled with water when it is not in use to minimise contamination. Before each use the material is rinsed again 8 times with ultrapure water.

Finally the microelectrode is inserted into our cylindrical glass cell that has been previously filled with electrolyte purged with N_2 (4.7 N). A first set of 3 cyclic voltammograms (50 mV s^{-1}; starting at 1 V going to 1.32 V then going down to 0.07 V and finishing at 1 V) is done to see the current range of the CV. If it fits with the expected values (for a 10 μm diameter electrode the current values are between 0.3 and −0.3 nA) then the electrochemical cleaning is started, if not, the electrode is again polished. The electrochemical cleaning consists of 250 cycles at 1 V s^{-1}; starting from 1 V going to 1.32 V then going down to 0.07 V and finishing at 1 V. The final shape of the CV is checked with 3 more cycles at 50 mV s^{-1}, where we carefully investigate the shapes of the H-upd peaks. If the peaks are well defined, then the electrolyte is saturated with CO, if not the electrode is polished again. In the CO saturated electrolyte, 20 cyclic voltammograms (50 mV s^{-1}; starting at 0.07 V going to 1.00 V then going down to 0.07 V and finishing at 0.07 V) are done to observe a stable CO diffusion limiting current and a sharp ignition peak. If the CVs are not stable, the electrode is sent back to polishing, if the CVs are stable, then the actual experiments are started.

Frederic Kanoufi asked: You are mentioning that the process is ruled by a characteristic length of the order of 10 micrometers, characteristic of an autocatalytic process whose apparent kinetics is then of the order of 10^3 s^{-1}. It is very nice that you proposed a deterministic simulation of the process, even though in 2D only. The simulation qualitatively reproduces the experimental bistability. Looking at the numbers you are using for this simulation, it appears that the desorption rate that you have chosen is of the order of 10^3 s^{-1}. I wonder if it is actually this desorption step which is rate determining. Is it maybe fortuitious? I wonder if this is fortuitious or if the same simulations can be obtained by changing k_{des} (for example to 1 order of magnitude higher)? Moreover, one has wondered if the bistability could be due to edge effects. I wonder if you could detect edge effects from your simulation (the edge of your insulating–UME boundary, although in 2D). We have indeed previously demonstrated that heterogeneous surface coverage could be detected both optically and by simulation at microelectrodes (edge *vs* center).[1] Would local monitoring (optically for example) be possible or helpful in your experimental situation?

[1] S. Munteanu, J. P. Roger, Y. Fedala, F. Amiot, C. Combellas, G. Tessier and F. Kanoufi, *Faraday Discuss.*, 2013, **164**, 241–258.

Katharina Krischer responded: Desorption does not play a role for the size of the critical nucleus. It is only taken into account to prevent total poisoning of the surface, *i.e.* a CO surface coverage of 1, which would not allow any reaction to occur. Since in experiments, CO oxidation occurs also when the CO adlayer is saturated, we allowed for some desorption of adsorbed CO molecules. Alternatively, we could have assumed that the maximum CO coverage is less than 1, *e.g.* 0.99, and omitted CO desorption completely. This still gives rise to a bistability. The characteristic length is determined by an interaction of reaction kinetics and diffusional coupling. The reaction rate in front of the bare domain is diffusion limited, and thus the CO concentration in front of the electrode is very small. In contrast, the reaction rate on the CO covered patch is negligibly small; the CO concentration in front of a CO covered surface is thus close to the bulk CO concentration. Consequently, CO molecules adjacent to the electrode diffuse from the CO covered domain to the bare surface, where they may adsorb and react. This is the principal mechanism that adjusts the width of the interface between a CO covered and a reactive domain, and also the critical nucleus. Note that compared to diffusion in the electrolyte, surface diffusion of adsorbed CO is much slower. Therefore, we believe that it does not contribute significantly to the interface width or the critical size of a nucleus. Hence, as answered to Prof. Schmickler's question a rough estimate of the radius of a critical nucleus is given by a combination of the diffusion coefficient and the reaction constant of CO oxidation. As for the second part of your question: our simulations assumed a semicircular electrode surrounded by electrolyte. Hence, the simulation does not take into account the UME–insulator transition. Still, the simulations reproduce the spontaneous formation of domains on the electrode surface. Therefore, they suggest that the domain formation is intrinsic to the dynamics and not induced by the edges. On the other hand, in the experiments the edges impose inhomogeneous parameter distributions and might have an influence where the domains nucleate. It would certainly be interesting to study the local CO coverage on the UME. However, optical imaging does not give any contrast. IR imaging would give the contrast, but it brings about further experimental difficulties. The only IR technique I am aware of that allows for spatial resolution is SEIRAS measurements,[1] and here the spatial resolution is on the order of some 10 microns, and thus not sufficient in our case.

[1] P. R. Bauer, A. Bonnefont and K. Krischer, *Sci. Rep.*, 2015, **5**, 16312.

Philip Bartlett remarked: The current distribution at the microelectrode can be non-uniform and at the edge there is a change in the double layer between that over the platinum and that over the glass insulation. As the microelectrode becomes smaller these edge effects might be expected to become more significant. Do you see any influence from the boundary between the platinum disc and the glass insulation in your experiments?

Katharina Krischer answered: *A priori*, it is not possible to see in the experiments whether the metal electrode–insulator transition has an impact on the phase transition we observe. However, in our simulations we assume a hemispherical metal electrode surrounded by electrolyte (except for the base plane). Hence, in the simulations we do not have inhomogeneities due to mixed boundaries. Since the inhomogeneous phase transition and the critical size of the nucleus as well as its dependence on the density of active surface sites are all well captured by the simulations, it is not necessary to consider the influence of the non-uniformities at the edge of the microelectrode to explain these phenomena. However, I could imagine that edge effects determine where a domain nucleates. It would certainly be interesting to do simulations with the mixed boundaries and compare them with those of the hemispherical electrode.

Kristina Tschulik commented: You mentioned that you observe an increase in the frequency with time. Do you assume that the origin of this effect is the co-adsorption of impurities from the electrolyte or that this is caused by the repeating phase transition in the course of the experiment? Both causes might be distinguished from each other by immersing the electrode in the electrolyte for several minutes prior to starting the experiment. If an increased frequency is observed then the first scenario seems likely, otherwise the second would likely be the origin.

Do you expect any influence of surface charge of the insulation sheath on the phase transition? If so the application of an electrophoretic paint instead of a glass sheath might be tested usefully.

Katharina Krischer responded: I would assume that the increase in frequency of, *e.g.*, the shot-noise-like spikes are due to a slow contamination of the electrode surface. But it would certainly be interesting to test it in the way you suggested, thanks for this comment. Concerning the influence of surface charge of the insulation sheath on the phase transition, I expect it to be of minor importance. It might determine where the bare electrode phase nucleates, but I do not expect any effect on the qualitative observations we report in the paper.

Richard Crooks asked: To what extent do you think solution impurities affect the types of measurements you make? I understand that you take precautions in this regard before experiments begin (*e.g.*, cycling the electrode until the signature of a clean Pt surface is observed), but no matter how much effort one puts into purifying water, there is still organic material present that can affect sensitive experiments like yours if it adsorbs to the surface AFTER initial electrode preparation. Could you comment on this possibility and the effect it might have on your observations?

Katharina Krischer answered: This is a very important aspect. It is clear that there will be always some contamination during the measurement. If you look, *e.g.*, at the time series measurements in our paper (Fig. 7 and 6), you observe a slow increase in potential with time. We attribute this increase to a slow and minor contamination of the surface (though it might also be due to the formation of Pt oxides with a higher valency that have a lower reactivity towards CO oxidation). The potential increase tends to be less pronounced the lower the current is, *i.e.* the larger the CO coverage is, which makes sense. However, looking at the figures it also becomes clear that the qualitative effects are not affected by the contamination: the critical electrode size clearly depends on the sulfuric acid concentration (compare *e.g.* the time series in Fig. 6a and Fig. 7a,b); the potential transients become noisy as soon as phase separation occurs, and so on. The main impact of contamination that I see on our measurements is that we are restricted in the length of the time series we can record. It would certainly be desirable to study the power spectra at lower frequencies since the different types of noise should have a different signature in the low frequency tail. But this is not possible due to the influence of minor contaminations.

Marc Koper asked: In relation to Dick Crooks' comment about electrolyte impurities: what would happen if you add small amounts of chloride to the electrolyte?

Katharina Krischer responded: In fact, the addition of chloride introduces a negative feedback into the reaction network rendering the local (or lumped) dynamics oscillatory.[1,2] Of course, whether oscillations are observed or not depends on the parameters of the system, most importantly the chloride concentration. We have just started to study the dynamics of CO oxidation in the presence of chloride on microelectrodes. The behavior is rather complex and we are still in the middle of our studies. But as a first, rough description I would say that for very low chloride concentrations one still observes the formation of two phases and corresponding fluctuations. At higher chloride concentrations, in addition to the random behavior, characteristic frequencies show up. Also the low frequency boundary up to which the $1/f^2$ scaling is observed is shifted to higher frequencies so that in this case it seems to be possible to evaluate it. But for the moment it is too early to make any further statements.

1 S. Malkhandi, A. Bonnefont and K. Krischer, *Surf. Sci.*, 2009, **603**(10–12), 1646–1651.
2 S. Malkhandi, P. R. Bauer, A. Bonnefont and K. Krischer, *Catal. Today*, 2013; **202**, 144–153.

Julie MacPherson opened a general discussion of the paper by Thom Hersbach: Given the importance of cation adsorption in the processes described, what is the role of cation size on the adsorption process, *e.g.* Li^+ versus Cs^+? Have you looked at anything other than Na^+? What do the DFT adsorption energy models predict?

Thom Hersbach responded: We have not explored any other cations in DFT. However, we are currently working on experiments that involve other cations, which show that the corrosion behavior can change when varying the cation. For example, initial experiments indicate that the corrosion preference of gold can be moved towards (100) when lithium is present in the solution.

Wolfgang Schuhmann asked: You used the term “onset potential” which is a physico-chemical undefined expression of a potential at which a reaction starts. Could you explain the meaning in your context? Which better expression would you propose?

Thom Hersbach replied: In our context, the onset potential is simply the earliest potential at which we can detect changes in the electrode surface. In other words, it is the least negative potential at which we can detect cathodic corrosion. The determination of this potential is limited by the accuracy of our equipment and our ability to reliably identify differences between voltammograms. This is the reason why we defined the onset potential with a 0.1 V accuracy and did not choose to use a more well-defined expression such as the standard equilibrium potential. But perhaps the most important limitation is that determining such a formally well-defined potential requires a lot more general understanding of cathodic corrosion than we have right now.

Wolfgang Schmickler remarked: During the 1980s the group of Arvia published a series of papers in which they showed that the surface of platinum can be modified by rapid cycling. Depending on the cycling rates and the potential range, they obtained different surface structures. Can your work be related to that of Arvia?

Thom Hersbach responded: Our work can certainly be related to that of the group of Arvia, in the sense that they were able to use an electrochemical method to roughen and preferentially orient an electrode. These electrodes even exhibit features that we observe on our electrodes, such as particles and well-defined etch pits. Arvia's approach differs from ours in the procedure and underlying chemistry: typically, a cycling procedure is used in which potentials above 0 V *vs.* RHE are applied. Since the upper potential limit is typically high, the underlying chemical processes are attributed to formation and reduction of various platinum oxide and hydroxide phases. In contrast, we modify our electrodes by applying constant potentials below 0 V *vs.* RHE. The underlying chemistry is thus strictly cathodic in our case, which is an important difference with Arvia's work.

Michael Eikerling asked: Coming back to the question asked before by Wolfgang Schuhmann, could you determine a proper equilibrium potential of the process instead of referring to a vaguely defined “onset potential”? What is limiting you to find the equilibrium potential?

Thom Hersbach responded: There are two important factors that prevent us from defining us an equilibrium potential, which is actually something we addressed in our publication on the cathodic corrosion of platinum.[1] First of all, one needs to know the identity of all involved reaction species. Currently, the exact nature of the corrosion intermediates is still one of the largest open questions regarding cathodic corrosion.

Secondly, after identifying all reaction species, one would need to accurately determine their concentrations. The main reaction intermediate seems to be so unstable that it decomposes instantly. This makes its concentration ill-defined and hard to measure, since one cannot simply wait until equilibrium establishes and then determine the concentration of all species.

Thus, a standard equilibrium potential cannot be determined until we learn more about these two key issues.

[1] T. J. P. Hersbach, A. I. Yanson and Marc T. M. Koper, *Nat. Commun.*, 2016, 7, 12653.

Marc Koper commented: As a clarification: during the cathodic treatment, there is a fixed negative potential, and at no moment there would be any surface oxidation. The voltammetry shown is taken in sulfuric acid after the cathodic treatment in alkaline solution, and is used to characterize the surface structure obtained from the cathodic treatment.

Richard Crooks questioned: With regard to cathodic corrosion, could the corroding species be single ion species such as Au^-?

Thom Hersbach responded: We typically describe the corrosion intermediates as anions, without specifying the exact nature of these anions. Though we do not know the exact nature of these intermediates, we like to think of them negatively charged metal clusters. Such clusters might be able to stabilize the negative charge amongst the atoms of which they are composed, much like post-transition metal polyanions found in Zintl phases. By doing so, they might be more stable than single ion species.

However, single ion species are still valid candidates for the unknown reaction intermediate. In fact, the existence of single transition metal ions such as Au^- and Ag^- has been reported in non-aqueous solvents.[1,2] Similarly, Pt^{2-} can be prepared in air- and moisture-free environments.[3] So even though we simply describe the intermediates as unknown anions and like to think of them as clusters, we cannot definitively point towards one species to be the mysterious anionic intermediate; metastable single ion species are certainly candidates we are considering.

[1] W. J. Peer and J. J. Lagowski, *J. Am. Chem. Soc.*, 1978, **100**, 6260–6261.
[2] N. E. Tran and J. J. Lagowski, *Inorg. Chem.*, 2001, **40**, 1067–1068.
[3] A. Karpov, J. Nuss, U. Wedig and M. Jansen, *Angew. Chem., Int. Ed.*, 2003, **42**, 4818–4821.

Frederic Kanoufi said: Indeed the formation Au^- anions has been demonstrated by Allen Bard in the late 1970s.[1] However this anion is formed at very negative potentials (close to that of solvated electron formation). Would you suggest that it could be responsible for Au cathodic corrosion in your alkaline aqueous solution?

Regarding cathodic corrosion of metals in non-aqueous solvents, the corrosion of Pt seems to proceed via the generation of negative Pt species as proposed by Simonet .[2] The role of cations (intercalation products) has also been evidenced. How would this compare to the corrosion of Au or Rh?

Then Pt corrosion was also evidenced in an aqueous environment; the role of reactive oxygen species, generated by reduction of oxygen, is of particular importance.[3] Does O_2 have any influence on your Au or Rh cathodic corrosion?

[1] T. H. Teherani, W. J. Peer, J. J. Lagowski and A. J. Bard, *J. Am. Chem. Soc.*, 1978, **100**, 7768–7770.
[2] J. Ghilane, C. Lagrost, M. Guilloux-Viry, J. Simonet, M. Delamar, C. Mangeney and P. Hapiot, *J. Phys. Chem. C*, 2007, **111**, 5701–5707.
[3] J.-M. Noël, Y. Yu and Michael V. Mirkin, *Langmuir*, 2013, **29**, 1346–1350.

Thom Hersbach answered: The potential for the formation of gold anions in ammonia is an important consideration concerning the identification of the cathodic corrosion intermediate. At a first glance, the standard potential of −2.3 V *vs.* $Ag/AgNO_3$ that Bard *et al.* report does not seem that far off from the onset potential of −1.6 V *vs.* NHE that we found for gold corrosion. In fact, this onset potential is undoubtedly more positive than the true equilibrium that underlies cathodic corrosion, due to the low concentration of intermediate species that likely is present.

Still, it would be better to calculate the standard electrode potential for the formation of Au^- in water. Unfortunately, calculating this potential using classical thermodynamic formulas is challenging without running simulations; it is difficult to accurately calculate the solvation energy of an Au^- from known thermodynamic values. So, while the equilibrium potential of Au^- is a valid concern, we currently do not understand our system well enough to determine this value in order to definitively rule out or confirm Au^- as an intermediate.

Your second question regards the intercalation of cations in the bulk metal. Though these modifications do occur at potentials similar to our cathodic corrosion potentials, it seems counterintuitive for this to be the reason behind cathodic corrosion; for corrosion to occur through this mechanism, it would require incorporation and subsequent leaching of a cation at the same potential. Additionally, the shape of the reported iono-platinic phases seems irregular and reduction of these phases is reported to recover the original platinum structure.[1] These observations contrast with the anisotropic shape and stability of the features created by cathodic corrosion. So though the same initial reduction of metal may underlie cathodic corrosion and the formation of these iono-platinic phases, I think it is unlikely that these phenomena have similar reaction mechanisms.

The final question relates to the role of oxygen in our system. We purge our electrolytes with 6.0 purity argon before all experiments for at least 30 minutes. Therefore, there should be no influence of oxygen in our corrosion experiments.

1 J. Ghilane, M. Guilloux-Viry, C. Lagrost, P. Hapiot and J. Simonet, *J. Phys. Chem. B.*, 2005, **109**, 14925–14931.

Simon Higgins asked: I wonder if it would be possible to use cathodic corrosion as a synthesis tool, by incorporating a suitable ligand (*e.g.* a phosphite or CO) into the electrolyte to coordinate to very low-valent metal centres, although perhaps also it would be necessary to change the solvent. If it's not possible to do the latter, one candidate might be cyanide; in the 1960's there was a lot of work on using cyanide as a ligand for surprisingly low oxidation state metal complexes in liquid ammonia, for example $[Ni(CN)_4]^{4-}$ and even (if I remember correctly) $[Ti(CN)_4]^{4-}$. Could you comment on this from your experience of the phenomenon?

Thom Hersbach responded: That sounds like an interesting strategy. Though I do not have any experience with creating metal complexes by using cathodic corrosion, I can comment on several requirements and possible pitfalls related to this strategy.

First of all, the success of this procedure will strongly depend on the nature of the cathodic corrosion intermediate; one will only be able to obtain single metal complexes if the intermediate species is a single ion, as opposed to a polyanion. Secondly, the charge of the metal center during coordination of the ligands is important. Negatively charged intermediates will likely repel negatively charged ligands, making such ligands unsuitable for capture of the metastable corrosion intermediate. However, it might be possible to capture single metal atoms in the stage between reduction of the anion and clustering of the atoms into nanoparticles. This rules out solvents like liquid ammonia, since they will likely stabilize the negative oxidation state of the metal.

Finally, the ligand will have to be stable at the reductive potentials that are related to cathodic corrosion. Kinetic stability might be sufficient, such that one could choose a ligand for which the reduction is catalyzed poorly on the metal that is to be captured.

Taking all of this into account and assuming I were to attempt a one-step synthesis, I would work in a CO-saturated water solution if the cathodic corrosion intermediate species are indeed single ions. Water, on the one hand, will facilitate oxidation of the intermediate to the zerovalent state. CO, on the other hand, is uncharged and should be able to approach the intermediate anion. This might improve the chances of capturing the ion before or immediately after its reduction.

Wolfgang Schmickler remarked: Since the cations play an important role, would it not be useful to investigate systematically the alkali ions, starting from Li and going down the periodic table?

Thom Hersbach replied: This would indeed be very useful and this is a project that we are currently working on.

Olaf Magnussen asked: Does the electrode microstructure, in particular grain boundaries, play an important role in this process? A related cathodic corrosion phenomenon is hydrogen embrittlement and here grain boundaries play a important role. Studies of Pt single crystals may help to provide insight on the mechanism, in particular on the role of undercoordinated metal sites.

Thom Hersbach replied: The electrode microstructure does seem to play a role in the corrosion process, since the corrosion features seem to be more pronounced around grain boundaries. However, these features are still visible all over the electrode, which is even the case on platinum.[1] Platinum can be flame annealed before the corrosion experiments and thus has significantly less grain boundaries than the gold and rhodium electrodes used in this study. So though corrosion seems to be easier around grain boundaries, these boundaries may not be as important for cathodic corrosion as they are in hydrogen embrittlement, where they facilitate diffusion of hydrogen into the bulk metal.

Nonetheless, single crystal studies would generate important insights into cathodic corrosion. At this point we have not attempted these studies yet; the experiments may lead to the destruction of the single crystals, which are quite expensive.

1 T. J. P. Hersbach, A. I. Yanson and Marc T. M. Koper, *Nat. Commun.*, 2016, 7, 12653.

Zhongqun Tian commented: The mechanism of the cathodic corrosion and the interfacial components are very complicated and it seems to be necessary to get the surface information at the molecular level. However, due to severe hydrogen bubble evolution from the probed surface, most surface spectroscopic methods cannot be applied. The most suitable way could be the use of ATR configuration-based optical measurements. The gold film electrode can be used for plasmon-enhanced IR and Raman spectroscopy. In addition to the fundamental aspect, what is the advantage in practical applications for cathodic corrosion in comparison with the traditional means, *e.g.*, anodic processes for roughening Au and Pt electrodes?

Thom Hersbach answered: If the cathodic corrosion intermediates are IR- or Raman-active, these spectroscopy techniques could be quite valuable. Regarding your second question: in my opinion, the main benefit of cathodic corrosion would be the surface selectivity. In case of the platinum electrodes we studied earlier, we are able to remove almost all (110)-type sites. A similarly pronounced selectivity might be possible for gold, rhodium and other metals if the right conditions are found. In that sense, cathodic corrosion might prove to be a versatile surface modification technique.

Frederic Kanoufi addressed Thom Hersbach and Olaf Magnussen: Continuing the comment of Professor Tian regarding optical *in situ* monitoring, the dynamics of the cathodic corrosion of Au and Rh seems rather slow and would fit the image acquisition rate of *in-situ* STM described in Magnussen's talk. Would such *in-situ* STM imaging be possible?

Thom Hersbach replied: We have considered doing *in-situ* STM during cathodic corrosion. STM would provide valuable information, but *in-situ* STM is currently hindered by experimental complexities that are introduced when working in an STM cell. For example, one would have to switch between 10 M NaOH and 0.5 M H_2SO_4 in the same cell, which may introduce contamination and safety issues.[1] We have therefore not attempted STM while using the approach that we have used so far to study corrosion.

One could consider doing true *in operando* STM while cathodically corroding the electrode, but this is difficult due to the large amounts of hydrogen that are formed during cathodic corrosion. This hydrogen will be reduced on the STM tip and interfere with the measurements. So, though STM would be quite interesting, challenges in the experimental design have so far prohibited us from carrying out such experiments.

1 T. J. P. Hersbach, A. I. Yanson and M. T. M. Koper, *Nat. Commun.*, 2016, 7, 12653.

Olaf Magnussen replied: Because cathodic corrosion occurs deep in the hydrogen evolution regime, *in situ* STM studies of this process might be difficult. First, this reaction might lead to very unstable imaging conditions and, second, hydrogen bubbles may be trapped between tip and sample, resulting in blocking access of the electrolyte to the imaged surface area.

David Fermin asked: Is it possible to use mass spectrometry in order to detect the intermediate species generated during cathodic corrosion, prior to the formation of nanoparticles? Perhaps in a configuration similar to differential electrochemical mass spectrometry.

Thom Hersbach responded: So far, the main challenge in identifying this intermediate species has been its instability. Mass spectrometry might alleviate this problem if the intermediate species is stable in the vacuum under which the spectrometer operates. Proper experimental design will be vital in such an experiment, since one would not want the intermediate to decompose before entering the mass spectrometry system. Additionally, transport of the intermediate species through the membrane and into the mass spectrometer is likely not trivial. However, mass spectrometry might be an interesting tool for analyzing the intermediate species *in-situ*, if such a setup is made compatible with the corrosion process.

David Fermin opened a general discussion of the papers by Olaf Magnussen, Katharina Krischer and Thom Hersbach: All these papers deal with phase formation and dissolution processes. What is the role of water and ions in these processes? It is clear that cations play a role in cathodic corrosion, while anions contribute to the size of the CO phases at the micro-electrode. Is water a spectator?

Thom Hersbach answered: Water is certainly not a spectator species during cathodic corrosion. In fact, it might be a special enabler of the process because it possesses two important properties. Firstly, water seems to allow for the bulk metallic electrode to be reduced and dissolved into a layer in the solution that is practically water-free because of the vigorous hydrogen evolution that takes place during cathodic corrosion.[1] Secondly, water is able to re-oxidize these reduced metal clusters when they encounter free water. Thus, water allows for electrode material to dissolve and then precipitate. Solvents that only possess the first property, such as ammonia, will simply dissolve stable metal anions like Au^-. In contrast, solvents that lack the first property will not be able to dissolve the electrode at all.

[1] A. I. Yanson, P. V. Antonov, P. Rodriguez and M. T. M. Koper, *Electrochim. Acta*, 2016, **112**, 913–918.

Katharina Krischer responded: This is a very good question. I believe that at least in sulfate containing aqueous electrolyte water is more than a spectator since it influences the adsorption of sulfate ions, which, as you also mentioned, plays a strong role for the critical domain size. To really answer this question, one would need to have a much better understanding of sulfate adsorption under reaction conditions, and thus of its interaction with the adsorption of CO and OH on the Pt surface, than we have at present. I am not sure whether our experimental or technical methods are advanced enough yet to study these aspects on an atomic scale.

Olaf Magnussen replied: Understanding the role of water in electrochemical processes is still a central challenge in interfacial electrochemistry. The group of Schmickler has recently shown by theoretical studies of metal electrodeposition that the compatibility of the ion hydration shells with the structure of interfacial water has tremendeous impact on the ion transfer kinetics.[1] Similar effects likely are relevant for many other electrochemical processes and need to be explored further.

1 L. M. C. Pinto, E. Spohr, P. Quaino, E. Santos and W. Schmickler, *Angew. Chem. Int. Ed.*, 2013, **52**, 7883.

Richard Nichols addressed Thom Hersbach: Going back to David Fermin's question about water: for your DFT calculations of sodium adsorption on the surface do you include any remaining solvated water with the adsorbed sodium ions? This would seem to be important since it is generally taken that alkali metal cations adsorb with at least some and maybe quite a lot of the water hydration intact, with the energetics of removal of solvated water being high.

Also there are papers on the electrodissolution of Pd, Rh and Pt electrodes which have analysed and detected metal dissolution into the electrolyte during potentiodynamic procedures. The metal ion concentration accumulating in the solution has been analysed by widely available atomic absorption spectrophotometery.[1] For your procedure do you envisage metal dissolution as complexes in solution to be a possibility?

1 R. Schumacher, W. Helbig, I. Haß, M. Wünsche and H. Meyer, *J. Electroanal. Chem.*, 1993, **354**(1–2), 59–70.

Thom Hersbach responded: Our DFT calculations do not include any solvated water. We are aware that solvated water can be an important factor during these calculations, but think it is unlikely that the explicit inclusion of remaining solvated water will affect the relative differences that we found. Regarding your second question: metastable metal complexes in solution, such as metal hydrides, are the final species that we think might be intermediates in cathodic corrosion. However, these complexes generally possess a positively charged metal atom and would therefore require the bulk metal to be oxidized in order to form. Because we operate under strongly reductive conditions, we think that such metal complexes might be less likely intermediates than anionic intermediates. *In-situ* studies shall have to shed light on this situation.

Richard Crooks addressed Olaf Magnussen: You didn't mention the possibility of tip-induced effects in your presentation. Back in the early 90s when my group worked in this field this was a serious problem, but perhaps things have changed. Are you able to rule out tip effects in the results you presented today, and if so how do you do that?

Olaf Magnussen replied: Tip effects are indeed an issue and have to be considered in every *in situ* STM experiment. Different types of such tip effects exist: First, the presence of the tip can block access of electrolyte species to the surface, which is in particular a problem for faradaic processes. As discussed in our paper, this leads to a significant reduction of the deposition rate underneath the tip, which is a well known phenomenon. Second, the tip may directly induce changes of the surface structure and dynamics. We typically perform experiments at different tunneling parameters to assess this influence. Because the surface is imaged in constant height mode in our video STM experiments, *i.e.* at a fixed average tip-sample distance, this is in particular problematic for freestanding high structural features on a planar surface, where this distance can become very small. An example are the Bi nanochains on Au(100), where the dynamic behaviour indeed may be significantly influenced by the tip and thus was not analysed quantitatively. In contrast, the kink dynamics along Bi steps is determined by processes on the lower terrace, where the tip-surface distance is large, and consequently is not noticeably affected. We note that only rather strong tip effects can influence these measurements of the dynamic fluctuations, since the tip is located only a short fraction of the time directly above the kink site.

Patrick Unwin commented: I'd like to pick up again on the point about what the tip does locally. There is a related AFM literature on crystal growth and dissolution which we have recently analysed.[1] For such nanoscale measurements, there is a tendency to focus on areas of the surface that are close to perfect, with just a few step edges, but when one deduces the kinetics from these measurements, they are typically one or more orders of magnitude slower than one might expect from macroscopic measurements. This is mainly due to flux processes outside the AFM scan area (region of interest) affecting the region of interest. The surfaces we tend to look at are very heterogeneous spatially, as are the interfacial fluxes, and as concentration boundary layers tend to extend by tens of microns (at least) above a surface, there is considerable diffusional cross-talk between neighbouring areas of a surface that needs to be taken into account to make kinetic measurements by scanned probe microscopy quantitative. Areas outside the scanned area tend to be rougher and more active and so have a substantial influence on the region of interest.

1. M. Peruffo, M. M. Mbogoro, M. Adobes-Vidal and P. R. Unwin, *J. Phys. Chem. C*, 2016, **120**(22), 12100–12112.

Olaf Magnussen answered: In order to monitor details at individual defects, such as crystal steps, high resolution STM/AFM requires that these defects are spaced at sufficient distances from each other. For a comparison of the microscopic and the macroscopic growth rate the ion transfer mechanism should play a role: If ion transfer occurs at defects (“direct deposition”) one would have to normalize by the defect density, which may be much higher on real electrode surfaces. If ion transfer proceeds *via* the formation of adatoms on the surface, subsequent nucleation and growth of islands of the deposit will occur and the local deposition rate will be independent of the initial defect density. In both cases, strong deviations between microscopic and macroscopic growth may occur, if mass transport in solution plays a significant role, because of the mentioned cross-talk between different electrode areas and the effect of the tip. This is a particularly serious problem for deposition processes with fast ion transfer, *e.g.* Cu electrodeposition.[1] In contrast, for processes with strongly inhibited ion transfer kinetics, such as Ni, Co, and Fe deposition, the microscopically observed deposition rates are often similar to those determined macroscopically.

1 O. Skylar, T. H. Treutler, N. Vlachopoulos and G. Wittstock, *Surf. Sci.*, 2005, **597**, 181.

David Fermin asked Olaf Magnussen: In your images, Bi nucleation and growth occur over a Bi monolayer on both Au surface orientations. Is this a general process? One would expect that the UPD will be unstable and reconstruct into 3D nuclei at potentials more negative than the Bi reduction potential (overpotential region). Can the Bi UPD layer be lifted upon positive polarization, or does it go through a spontaneous irreversible adsorption?

Olaf Magnussen replied: It is difficult to judge on the basis of the STM experiments whether the structure of the Bi UPD layer is maintained underneath the Bi bulk deposit or whether this layer is restructured into a bulk-like lattice. This could in principle be clarified by surface X-ray diffraction methods, but corresponding data for Bi on Au(111) and Au(100) has not been published so far. However, that a bulk deposit can grow epitaxially on top of a UPD layer, whose structure is maintained underneath, has been obeserved in other systems, *e.g.* for Tl on Ag(100).[1] Regarding the second question, the Bi OPD as well as UPD is highly reversible. Positive polarization results in fast dissolution/desorption of Bi from the Au surface.

1 J. X. Wang, R. R. Adžić, O. M. Magnussen and B. M. Ocko, *Surf. Sci.*, 1995, **344**, 111.

Julie MacPherson returned to discussion of the paper by Thom Hersbach: Why choose 10M sodium hydroxide as the electrolyte for all these studies, it seems an extreme medium?

Thom Hersbach replied: Indeed, 10 molar is quite a high concentration. Though lower concentrations also allow for cathodic corrosion to take place, the corrosion process is most pronounced at these high concentrations. Since the changes caused by cathodic corrosion are more apparent, using such a high concentration thus facilitates their detection. This in turn allows for a more reliable definition of the onset potential.

It is worth mentioning that we are currently working on experiments in less concentrated electrolytes and the first data indicate that, for the systems we have tested so far, the onset potential does not shift negatively by more than 100 mV on the RHE scale.

Marc Koper added: The reason for using (strongly) alkaline media is partially historical, as this is the medium in which Pt wires are etched to make STM tips, and this is how we (re-)discovered the phenomenon of cathodic corrosion. Note, however, that during cathodic corrosion, strong hydrogen evolution generates a condition of high alkalinity near the electrode surface. Therefore, the exact bulk pH does not matter for the phenomenon,[1] and the local surface condition is always highly alkaline.

1 A. I. Yanson, P. Rodriguez, N. Garcia-Araez, R. V. Mom, F. D. Tichelaar and M. T. M. Koper, *Angew. Chem. Int. Ed.*, 2011, **50**, 6346.

Michael Eikerling opened a general discussion of the paper by Henry White: In your article as well as your presentation, you suggest that bubbles nucleate in the bulk solution, away from the catalyst surface. What evidence do you have for bulk nucleation as compared to surface-catalyzed heterogeneous nucleation (which seems the more likely option to me)? Looking at the sensitivity of the nucleation kinetics to the surface structure of the catalyst should provide valuable insight in this regard. Has this been explored experimentally?

Henry White responded: We would expect that differing roughness and/or hydrophobicity of the electrode surface should have dramatic effects upon the critical concentration if it were a surface catalyzed process. We are not able to explicitly control the structure of the electrode surface in these experiments. Therefore, the reproducibility of the critical concentration for nucleation electrode to electrode is surprising and is the main reason we suggest the nucleation we observe is homogeneous. Ultimately, we do not know whether nucleation in this case is surface catalyzed or not.

Olaf Magnussen commented: I would be interested in the case of heterogeneous bubble nucleation at the electrode surface. Because the gas concentration is highest directly at the surface, this should be considered. I agree with the authors that the general form of the equations and the analysis will be the same. Also in this case the free energy contribution of the volume will scale as r^3 and that of the bubble surface as r^2. However, the prefactors will depend on the wetting angle θ. Specifically, the latter term will have a contribution from the electrode–gas interface with a surface energy term given by the difference of the solid–gas and the solid–liquid interface tension, which can be calculated by the Young's equation as $\gamma \cos(\theta)$. Also the solid–liquid interface area and the bubble volume will depend on θ. Consequently, also the critical radius and the free energy barrier E_aa should vary with θ. I assume that these effects have been discussed previously in the literature. Could the authors comment on this? In particular, I would be interested whether with increasing wetting angle a crossover between homogeneous and heterogeneous nucleation is expected.

Henry White replied: We agree with the above in principle. Whether the nucleation we observe is homogeneous or heterogeneous is unknown. As pointed out in the article, the radius of curvature of the critical nucleus is unaffected by the mechanism. The classical theory for the rate of heterogeneous nucleation of bubbles is $J = Z\exp\left(\dfrac{-16\pi\gamma^3\Phi(\theta)}{3kT(P_{\text{gas}} - P_{\text{ambient}})^2}\right)$. where Φ is a function of the contact angle, θ, given by $\Phi(\theta) = \frac{1}{4}(1 + \cos\theta)^2(2 \neg \cos\theta)$. For a contact angle of 0 degrees (measured through the liquid) $\Phi(\theta) = 1$ and the equation for homogeneous nucleation obtains.

Patrick Unwin commented: There is a growing literature and evidence of the importance of non-classical nucleation and growth processes, for example, in the growth of organic and inorganic materials[1] and metal nanoparticles (aggregative growth processes)[2–5], in which growth is by small clusters and aggregates coming together. Could such processes operate in nanobubble nucelation? Given the current magnitudes measured in these experiments, it should be possible to make dynamic measurements on quite a fast timescale (perhaps 100 kHz or better). Have you tried to make fast current–time measurements and, if so, do they provide any insights on the bubble nucleation and growth mechanism, for example, the dynamics of pre-nucleation cluster formation/dissolution?

1 P. R. Unwin, *Faraday Discuss.*, 2007, **136**, 409–416.
2 J. Ustarroz, X. Ke, A. Hubin, S. Bals and H. Terryn, *J. Phys. Chem. C*, 2012, **116**, 2322–2329.

3 J. Ustarroz, J. A. Hammons, T. Altantzis, A. Hubin, S. Bals and H. Terryn, *J. Am. Chem. Soc.*, 2013, **135**, 11550–11561.
4 S. C. S. Lai, R. A. Lazenby, P. M. Kirkman and P. R. Unwin, *Chem. Sci.*, 2015, **6**, 1126–1138.
5 Y.-R. Kim, S. C. S. Lai, K. McKelvey, G. Zhang, D. Perry, T. S. Miller and P. R. Unwin, *J. Phys. Chem. C*, 2015, **119**, 17389–17397.

Henry White responded: Bubble growth by nucleus aggregation is certainly possible. We are thankful for the educational list of references from the Unwin group in that regard although none of these articles noted by Professor Unwin actually describe gas bubble nucleation. We are currently studying rates of bubble nucleation at high recording frequencies that may shed additional light on these non-classical processes.

Andrew Ewing said: I think contact angle won't matter with huge pressure, and you say the gas covers the whole electrode. Is this correct? How do you measure pressure in the dynamic *vs* static case? Don't you have to take into account that hydrogen is flowing out of the bubble? Shouldn't there be a dynamic equilibrium between the hydrogen bubble and pressure of hydrogen in solution? How do you take this all in to account? Do you have to know the diffusional flux? Can you put this in context of where this would be something we could use for something else and what the interest is in this process?

Henry White answered: We believe the bubble covers nearly the entire electrode only after nucleation and growth when it reaches a steady-state size limited by the size of the electrode. Indeed, the bubble growth and dissolution are controlled by diffusional flux while the concentration at the bubble surface is determined by Henry's Law for equilibrium with the bubble's internal pressure. Further clarification on this dynamic equilibrium can be found in our previous work.[1–4] Nanobubbles have attracted attention for their applications in slip enhancement in fluidic channels, surface cleaning, froth flotation, templating nanomaterials, and as propulsion for nanodevices. Gaining an understanding of the nucleation processes and control over nanobubble localization and growth will be critical for these future developments. This knowledge will also aid the prevention of bubble formation where it can have adverse consequences as in cavitation, decompression sickness, and disruption of electrode processes in batteries and fuel cells.

1 L. Luo and H. S. White, *Langmuir*, 2013, **29**, 11169.
2 Q. Chen, L. Luo, H. Faraji, S. W. Feldberg and H. S. White, *J. Phys. Chem. Lett.*, 2014, **5**, 3539.
3 Q. Chen, H. S. Wiedenroth, S. R. German and H. S. White, *J. Am. Chem. Soc.*, 2015, **137**, 12064.
4 S. R. German, Q. Chen, M. A. Edwards and H. S. White, *J. Electrochem. Soc.*, 2016, **163**, 3160.

Patrick Unwin opened a general discussion of the paper by Jan Clausmeyer: In Fig. 3 of your paper you showed that many Ag nanoparticles and clusters were on the glass sheath around the carbon nanolectrode, but you were unsure about how they formed. I believe your observations are consistent with our recent measurements of silver nucleation and growth on highly oriented pyrolytic graphite (HOPG) electrodes,[1] where we showed that silver nanoparticles grew initially via the aggregation of silver ad-clusters, but that the nanoparticles detached from the surface after a few milliseconds (after reaching a size of about 25–30 nm in diameter). This process was characterised by a very regular periodicity for nucleation–growth–detachment (*ca.* 100 Hz). You see nanoparticles of about the same size around the nanoelectrode and I suspect they are formed on the electrode but detach and stick preferentially at the glass. So, your experiments lend further support to our mechanism. It would be interesting to run chronoamperometric measurements and see if you observe similar features.

1 S. C. S. Lai, R. A. Lazenby, P. M. Kirkman and P. R. Unwin, *Chem. Sci.*, 2015, **6**, 1126–1138.

Jan Clausmeyer replied: Yes, this observation matches our findings in a number of aspects. For instance, when we deposit silver at low overpotential, low silver ion concentration and for short times, the predominant nanoparticle size we obtain is consistent with the results in your paper. This is very interesting with regard to the electrosynthesis of nanoparticles with controlled size and shape. What factors influence the growth and detachment and thus the particle size? How could one use this to control the particle geometry?

However, in one respect our findings are different from what you observed: For long deposition times (many seconds) we do not see a periodic behavior of the cathodic current but rather a steady increase. As a result, the Ag clusters on the nanoelectrode get a cauliflower-like shape. This might be due to different mass transport rates for the two different experimental configurations, namely almost spherical diffusion for Ag growth on a pointy nanoelectrode *vs.* rather linear diffusion for Ag growth in the scanning capillary configuration in your work.

Julie MacPherson asked: First, have you looked at how the cathodic deposition current correlates with the anodic stripping current for Ag deposition and stripping? Assuming nothing else is going on cathodically then a larger cathodic current would support Pat Unwin's comment about Ag particle movement away from the electrode.

Second, given the previous discussions throughout the meeting on the use of TEM, this would be a much better technique for you to use than SEM as a means of assessing Ag particle size, have you considered using it?

Third, it was not clear what size C electrodes you are using. You just talk about a 10 pA current in the paper, can you comment further?

Jan Clausmeyer replied: Answering your first question: we have tried to correlate the transmitted charge for cathodic metal deposition with the charge of Ag stripping peaks and found that the deposition charge is consistently larger than one would expect when looking at the size of the deposited particles. In a different context we have made the same observation for the deposition of Au particles on nanoelectrodes. It seems to be a general phenomenon that any cathodically reduced material is very likely to escape from the electrode, bearing in mind that mass transport is very fast at such small electrode dimensions and that the interaction between the carbon material and the metal particles might be weak. Patrick Unwin's comment and our findings are in very good agreement with this picture.

Answering your second question: yes, there are a small number of papers proposing TEM as a tool for characterization of nanoelectrodes. We expect that

TEM analysis will improve the estimation of size and geometry of the electrodeposited metal clusters and reduce the uncertainty concerning the exact geometry of the dual barrel nanoelectrodes. We will try to establish TEM as a routine characterization tool for studies related to nanoelectrodes in future work.

Answering your third question: estimating the size of nanoelectrodes based on electrochemical data and electron microscopy data (see above) is not trivial. The common practice is to estimate the size from steady-state voltammograms, complemented by some electron micrographs. We believe that one should be very careful with making bold statements about the electrode size based on electrochemical data because, first, one needs to assume that electrodes are disk-shaped and co-planar with the insulating shield and, second, that classical continuum description of mass transport is valid at such dimensions. The latter point is addressed by Shengli Chen's paper presented in this Faraday discussion and earlier work.[1] For the nanoelectrodes used in our paper, which are made from Θ-shaped capillaries, it is very unlikely that they have a disk-shaped geometry. Hence, we only report the steady-state voltammetric currents to refer to a roughly estimated size. The 10 pA reported in the manuscript correspond to an electrode diameter of about 10 nm, if they were disk-shaped.

1 S. Chen and Y. Liu, *Phys. Chem. Chem. Phys.*, 2013, **16**, 635–652.

Christine Kranz asked: Could you please comment on the error bars in Fig. 6b of your manuscript? The measurements indicate that there is no significant difference for the different NaOH concentration given the huge standard deviations. Also this might be even more true for the lower concentration if more measurements would have been conducted, n = 2 seems very limited. Error bars should only reported for the same number of measurements. The general definition of “error bar” should be considered, otherwise it is confusing, if the standard deviation is not reported. Were repeat measurements conducted at the same electrode? What is the stability of individual Ag-nanocluster modified nanoelectrodes under the described conditions?

Jan Clausmeyer replied: Fig. 6b compares results obtained with different electrodes. The large error bars are a result of both the small number of experiments as well as some experimental uncertainty in the preparation and modification of the nanoelectrodes. Variations and some extent of uncertainty in the electrode geometry are inherent to any kind of nanofabrication protocol and can never be avoided, not even with high technical effort. The Ag nanoclusters are electrochemically stable for the typical time frame of the experiment (*i.e.* the voltammetric curves remained stable). However, due to mechanical instability of the single clusters attached to the nanoelectrodes, the probability of detachment increases with each time the electrode is transferred between different solutions. A possible solution would be to bury the Ag cluster in slight nanocavities.[1] Before validating a quantitative model that explains ORR currents at different electrolyte compositions, certainly more experiments would have to be performed. The aim of the present paper was to establish a new analytical technique to study mass and electron transfer at the three-phase boundary and to investigate electrochemical reactions at non-mass transport-limited conditions – until now, qualitatively.

1 J. Clausmeyer, P. Actis, A. López Córdoba, Y. Korchev and W. Schuhmann, *Electrochem. Commun.*, 2014, **40**, 28–30.

Thom Hersbach commented: In Fig. 6b, you display the oxygen reduction activity enhancement that occurs when increasing the oxygen concentration. This enhancement is largest at the intermediate electrolyte concentration of 5 M. In the article, you mention that this cannot just be explained by slower oxygen diffusivity at higher alkalinity; you tentatively suggest other factors that might influence the enhanced activity, such as a changing meniscus shape at higher NaOH concentrations. Can you elaborate on this and explain why you expect an optimum activity enhancement around concentrations of 5 M NaOH? Does an optimum occur because the changing meniscus shape counteracts the slower oxygen diffusivity?

Jan Clausmeyer responded: Yes, the height of a meniscus in a capillary depends on the surface tension, the contact angle and the density of the liquid – all quantities which are themselves functions of the NaOH concentration. We have evaluated the meniscus heights by just immersing quartz glass capillaries into the different solutions and found that the meniscus rose least in the case of 5 M NaOH. Hence, at this concentration the distance between the gas–liquid interface and the silver nanoparticle is shortest, which may explain the high ORR currents. The message is that one also needs to take into account hydrodynamics when trying to achieve an optimal current density. This is true for the present experimental configuration based on nanoelectrodes but in particular also for industrial porous gas diffusion electrodes.

Zhongqun Tian commented: The electrical conductivity of the electrolyte is not linearly related to the concentration. The highest concentration does not mean the highest conductivity. The maximum conductivity of concentration of NaOH, KOH and H_2SO_4 is around 5, 6 and 7 mol l^{-1} respectively in aqueous solution. For the even higher concentrations, the conductivity decreases significantly, because of the formation of an ion pair consisting of a cation and anion, which is neutral and does not contribute to the conductivity. There are no free water molecules in the solution and even the solvated water molecules are not enough. So cations and anions can contact with each other to form the neutral ion pair; the physicochemical properties of this kind of electrolyte solution are very unique and complex. Therefore the electrochemical behavior of 10 mol l^{-1} may not be better than the 5 mol l^{-1} system.

Jan Clausmeyer replied: Considering that the absolute currents for the ORR at the nanoelectrodes are very small (pA range), we do not expect the electric potential drop in solution to have a large impact on the electrocatalytic turnover. This is probably true for all methods involving micro- or nanoelectrodes for electrocatalytic studies. However, the point raised is very valid for a different reason: water is consumed as a reactant in the ORR. Taking into account that all water molecules are tied to the ions in an incomplete solvation shell (only ~2 water molecules are nominally available per ion) and thus there is very little or no free water, it is even more surprising how the ORR can run at high current densities. The formation of ion pairs may free some water molecules and is probably part of the answer to that question.

Wolfgang Schmickler opened a general discussion of the paper by Shengli Chen: During the 1980s Blum and Henderson modelled the electrolyte as an ensemble of hard spheres with charges (ions) or with dipole moments (solvent). Two important conclusions can be drawn from this model: first, the size of the solvent molecules is more important than that of the ions. Second, there is no special Stern layer. The latter is corroborated by computer simulations. Could you explain why you focus on the size of the ions, and why your model contains a Stern layer?

Shengli Chen answered: This is a very good point. Indeed, the sizes of the solvent molecules are very important. Due to the solvation effect, the sizes of different ions could be averaged. In our model, we actually include the size of the solvent molecules. When we consider the size of ions, we actually use the values for solvated ions. In this study, we focus on how the volume exclusion of electrolyte ions and their solvation shells as a whole affects the electric-double-layer structure and voltammetric responses of nanometer-sized electrodes. We don't emphasize any specific ions. As mentioned in our paper, the two sizes we have considered represent the typical sizes of the electrolyte ions in aqueous and organic media.

As for the Stern layer, we still believe there is a Stern layer (compact layer) adjacent to the electrode surface due to the interactions between electrode and solvent dipoles and the strong interaction between electrode charges and solvated counter ions.

Patrick Unwin asked: You have outlined the assumptions and approximations in the model. Referring to Fig. 1 in your manuscript, could you comment further on the implications of extending the double layer from the electrode over the (glass) sheath surrounding it, given that the glass may be (heavily) charged,[1] and – in reality – the double layer at that location will usually be different to that over the electrode.

[1] See for example: D. Perry, R. Al Botros, D. Momotenko, S. L. Kinnear and P. R. Unwin, *ACS Nano*, 2015, **9**, 7266–7276.

Shengli Chen replied: This is a very expert comment and I agree with you on this point. In our model, it has been assumed that the glass sheath bears an identical compact double layer on its surface to that on the electrode surface, that is, both electrode and sheath surfaces bear a closely packed solvent dipole layer, adjacent which there is a closely packed solvated ion layer. We have to admit that this is a rather rough approximation. In a given electrolyte solution, the glass sheath surface would be fixedly charged; while the nature and density of charge on the electrode surface vary with potential. Therefore, the electric double layer above the glass sheath could be different to that on electrode. This would affect the ion profile in the region of the electrode edges. To this end, the results in this study may only qualitatively describe the effect of ion sizes on the double layer structures and voltammetric responses of nanoelectrodes. More detailed and accurate interfacial models should be used to get more quantitative information.

Henry White commented: Professor Shengli Chen's talk focused on the effect of interfacial electrical fields on ion transport and the observable current–voltage behavior of nanoscale electrochemical systems. This is a very different problem from previous theoretical work in 80s and 90s that focused more on the equilibrium interfacial structure using more atomistic modeling. Both are very challenging and important. There are a number of recent experimental systems of broad interest involving electron-transfer and ion transport within electric double layers in which we do not have a complete understanding. For instance, ion current rectification is observed in nanopores filled with aqueous electrolyte. Current theory suggests no rectification should be observed for systems in which the Debye thickness is much smaller than the radius of the nanopore, but experimentally, rectification is frequently reported under these conditions.[1] The importance of the electric double layer on transport is also amplified in the "Lemay thin-layer electrochemical cells", where the double layer can extend an appreciable distance across the electrolyte separating the two electrodes. These fields can have a dramatic influence on transport of redox molecules, even at moderate ionic strengths, as demonstrated in some of our recent work.[2–4] I believe that Professor Chen's work using continuum models is vital to understanding types of phenomena.

1 W.-J. Lan, M. A. Edwards, L. Luo, R. T. Perera, X. Wu, C. R. Martin and H. S. White, *Acc. Chem. Res.*, 2016, **49**, 2605–2613.
2 Q. Chen, K. McKelvey, M. A. Edwards and H. S. White, *J. Phys. Chem. C*, 2016, **120**, 17251–17260.
3 J. Xiong, Q. Chen, M. A. Edwards and H. S. White, *ACS Nano*, 2015, **9**, 8520–8529.
4 L. Fan, Y. Liu, J. Xiong, H. S. White and S. Chen, *ACS Nano*, 2014, **8**, 10426–10436.

Shengli Chen answered: It's pleasing that this theoretical work can receive such a positive comment. I agree with Professor White that the EDL would have much more pronounced effect on charge transfer and transport under nonequilibrium (dynamic) conditions than that expected from the equilibrium EDL models, especially in nanoscale interfacial electrochemical systems. There have been numerous theoretical and simulation works dealing with these problems during the last two decades. However, most of them have employed continuum equations and neglected the finite volumes of ions which could be very important at nanoscale electrochemical interfaces. This Faraday Discussion paper presents our preliminary results on how the finite sizes of ions impact the EDL structure and reactivity at the nanoscale electrochemical interface.

Philip Bartlett opened a general discussion of the papers by Jan Clausmeyer, Henry White and Shengli Chen, with a question for Henry White: The contact angle picture presented by Prof. Magnussen is reasonable but in practice experimentally contact angles can be quite irreproducible, with significant hysteresis between advancing and receding contact angle. Do you know how the bubble dissolves? In the literature, as I'm sure you are aware, there is much discussion of long lived nanobubbles and the presence of pancake shape nanobubbles on hydrophobic surfaces (see for example the review by Lhose and Zhang[1]). How quickly do your bubbles dissolve? Do they remain pinned at the glass/Pt interface as the hydrogen dissolves? Can you say anything about the capacitance current as the bubble dissolves?

In our experiments using regular structured surfaces on the micron scale we find that the gas bubbles nucleate on the adjacent insulating, hydrophobic, surface rather than on the metal; this is also seen in the literature (e.g. see Bussieux *et al.*[2]). Do you see any evidence for the bubble forming on the surrounding insulation rather than on the platinum electrode?

[1] D. Lohse and X. Zhang, *Rev. Mod. Phys.*, 2015, **87**, 981.
[2] C. Brussieux, P. Viers, H. Roustan and M. Rakib, *Electrochim. Acta*, 2011, **56**, 7194.

Henry White answered: The measured lifetimes (tens of milliseconds) of bubbles in our experimental system are 2–3 orders of magnitude longer than diffusion controlled theory predicts assuming either a pinned contact radius or a constant contact angle. We attribute the long lifetimes to a kinetic limitation of gas transfer and/or a mass transport resistance due to a recessed electrode geometry.

In our experiments, the surrounding insulator is glass and we do not anticipate, due to its hydrophilicity, that the bubbles would nucleate there. We do not know if the bubble remains pinned at the electrode insulator boundary as it dissolves. Experiments are being carried out to image the bubbles with atomic force microscopy that could help answer these questions. We have not measured a capacitive current as the bubble dissolves.

Sanli Faez remarked: Orrit and coworkers have measured dynamics of the generation and collapse of a nano-bubble initiated at a single gold nanoparticle with photo-thermal microscopy.[1] Knowing that the generation and collapse process can be so fast, a few nanoseconds, is it possible that the formation of small bubbles is left unnoticed in electrical current measurements?

[1] L. Hou, M. Yorulmaz, N. R. Verhart and M. Orrit, *New J. Phys.*, 2015, **17**, 013050.

Henry White responded: Compared with thermally generated vapor bubbles, bubbles nucleated from dissolved gas exhibit slower growth and dissolution rates because they are governed by diffusion of the gas in solution. Nevertheless, these bubbles are still expected to have short lifetimes on the order of micro- to milliseconds. Observation of bubble signatures in electrochemistry depends first on the bandwidth of the electronic instrumentation and secondly, on the effect of bubbles on the electrochemical current. When recording at a ~50kHz and 10kHz filter frequency we observe a smoothly increasing current with minimal noise followed by a single drop indicative of the bubble covering a significant portion of the electrode. We cannot rule out possibility of the formation of bubbles too small/short-lived to observe electrochemically.

Kristina Tschulik asked: Regarding the reduced shrinkage rate you observed for the hydrogen nanobubbles, how sure are your that the Pt electrode does not serve as a hydrogen reservoir, *i.e.*is the solubility of hydrogen in Pt negligibly small, despite the high internal H_2 pressure and the applied potential? Recently we observed that the relaxation of the open circuit potential (OCP) with time after hydrogen bubble formation may reveal if the bubble remains attached to the electrode or not.[1] In this case, however, the micrometric electrode and bubble size allowed us to additionally follow the bubble shrinkage by optical means. Did you observe any similar features of the OCP time response that could reveal if a nano bubble is attached to your nanoelectrode? If so, could this serve as a measure at which minimum radius the bubble shrinkage makes it collapses?

1 F. Karnbach, X. Yang, G. Mutschke, J. Fröhlich, J. Eckert, A. Gebert, K. Tschulik, M. Uhlemann and K. Eckert, *J. Phys. Chem. C*, 2016 **120**, 15137–15146.

Henry White responded: Recently, we reported bubble lifetimes 2–3 orders of magnitude longer than diffusion-controlled theory predicts.[1] We do not attribute the longevity of the bubbles to a reservoir of dissolved hydrogen within the Pt electrode because, in contrast with Pd, hydrogen solubility is extremely low in Pt. We believe the long lifetimes to be affected more by kinetic limitations of gas transfer and/or mass transport resistance due to a recessed electrode geometry. The transient OCP response after bubble formation has not been studied in our experimental system, but we expect it would require an extremely high input impedance to record in nanoelectrode systems.

1 S. R. German, Q. Chen, M. A. Edwards and H. S. White, *J. Electrochem. Soc.*, 2016, **163**, 3160.

Sushanta Mitra returned to the paper by Shengli Chen: If one writes the free-energy for the problem, it will become evident that the ion size effect, entropic effect of ions, and solvent polarization are key contributions. Please refer to series of publications from our group.[1–2]

1 S. Das, S. Chakraborty and S. K. Mitra, *Phys. Rev. E*, 2012, **85**, 051508.
2 R. Mishra, S. Das and S. K. Mitra, *J. Chem. Phys.*, 2013, **138**, 114703.

Shengli Chen replied: You are totally right. In our model, we don't include the solvent polarization in the free energy formulation. What we are mainly concerned with is how the ion volume exclusion may affect the electric double layer structure and voltammetric responses. We have not attempted to give a comprehensive and accurate description of the electric double layer structure. So, we have ignored other possible contributions to the free energy at the interface. But the solvent polarization should be an important issue and it should be related to the ion sizes. Thank you for pointing out this and the references, we will look at them to improve our models in future works.

Andrew Mount addressed Henry White: The evidence in this work is that nanobubble formation is only weakly dependent on the nature of the gas. One driver to gas nanobubble formation and growth could therefore be the drive to minimise gas volume so as to maximise solvent–solvent intermolecular bonding (*i.e.* with the process being driven by maximising favourable solvent–solvent interactions). Have the authors carried out work *e.g.* on D_2 formation in D_2O systems and how does/would this give insight into the relative contributions of kinetics and thermodynamics to nanobubble nucleation and growth?

Henry White responded: Interestingly, the classical theory does not predict any dependence upon gas type. Instead, as the question suggests, the solution surface tension and the gas supersaturation are the dominant variables. We have not worked with the D_2/D_2O system; however, we are currently studying bubble nucleation in other solvents to further understand the process.

Michael Eikerling addresed Jan Clausmeyer: The triple-phase boundary is an ideal construction (a singularity). In your experimental system, what is the actual distribution of dissolved oxygen in the electrolyte surrounding the electrode? This distribution would determine the active surface area fraction of the electrode (and an effectiveness factor of surface area utilization). For a simple estimation, have you evaluated the diffusion length (or the reaction penetration depth) of oxygen in the electrolyte under the given experimental conditions? An estimate for this property could be easily obtained if the diffusion coefficient of oxygen in the electrolyte were known. Could you provide a value of this diffusion coefficient?

Jan Clausmeyer answered: Yes, oxygen is probably transported over a thin electrolyte film separating the gas phase and the solid catalyst. Unfortunately, we do not know the exact position of the gas–liquid interface with respect to the orifice of the nanocapillary. The diffusion coefficient in highly concentrated NaOH solution is in the range of some 10^7 cm^2 s^{-1} (for instance 8×10^7 cm^2 s^{-1} in 10 M NaOH.[1])[1] Based on that, the oxygen diffusion layer may still reach many micrometers into the solution. In ongoing experiments we are addressing this question using Scanning Electrochemical Microscopy (SECM). By approaching nanoelectrodes to gas diffusion electrodes one can determine both the diffusion length of oxygen around gas channels as well as the thickness of the depletion layer around electroactive catalyst domains.

1 C. Zhang, F.-R. F. Fan and A. J. Bard, *J. Am. Chem. Soc.*, 2009, **131**, 177–181.

Patrick Unwin asked: Have you thought about using a different configuration, for example, a theta pipette with an electrolyte-filled channel as an SICM distance sensor and an oxygen-delivery channel that you could bring up to a single nanoparticle on a surface or group of nanoparticles? This would seem to offer a well-defined arrangement for quantitative analysis.

Jan Clausmeyer replied: Yes, that would be a very good experimental arrangement which would allow the distance between the gas-liquid interface and the solid catalyst to be controlled with high precision and thus allow the oxygen diffusion layers to be imaged under these conditions. In fact, those experiments are currently ongoing in our laboratory. Several configurations are possible: first, approaching a double-barrel pipette with one oxygen-filled barrel under SICM control to Ag nanoparticles, second, approaching a Ag-modified nanoelectrode to an oxygen-permeable membrane and third, approaching an oxygen nanosensor to a gas diffusion electrode comprising both oxygen channels and catalyst spots. The presented work was only the first step in a series of different experimental approaches. Its advantage is that it does not require sophisticated positioning devices and software but only a laser puller and some tubing.

Wojciech Nogala asked Henry White: The number of molecules in the critical nucleus is calculated using the ideal gas law, assuming ambient temperature. Formation of gas bubbles on a gas-evolving electrode resembles cavitation.

The temperature of cavitating vapor bubbles differs significantly from the ambient temperature.[1,2] Is it possible that the formation of critical nuclei from an electrogenerated (supersaturated) gas solution, their growth and possible shrinking and collapse are adiabatic processes rather than isothermal? Then the temperature and the number of molecules would be different.

[1] F. Lugli and F. Zerbetto, *Phys. Chem. Chem. Phys.*, 2007, **9**, 2447–2456
[2] E. B. Flint and K. S. Suslick, *Science*, 1991, **253**(5026), 1397–1399.

Henry White responded: Rates of cavitation/evaporation and collapse/condensation of vapor bubbles are quite different from the growth and dissolution of gas-filled bubbles controlled by diffusion. The heats of vaporization and rate at which evaporation/condensation occur are extreme for vapor bubbles such that thermal diffusivity in water cannot maintain isothermal conditions. Because the bubbles we study are controlled by diffusive rates of gas in solution which is much lower than thermal diffusivity, we assume that nearly isothermal conditions are maintained. However, we do not have an experimental measure of temperature in our system and cannot be certain.

Frederic Kanoufi communicated: The pressure inside the nanobubbles is so high that I wonder if for certain systems you cannot evidence the formation of supercritical fluid droplets, for example with CO_2?

Henry White communicated in reply: We are aware that the formation of supercritical fluid droplets is an intriguing possibility. To date our studies of CO_2 bubbles have been hampered by the gases' high solubility and the concurrent generation of other gases. We are working to find the right conditions under which purely CO_2 bubbles can be nucleated.