

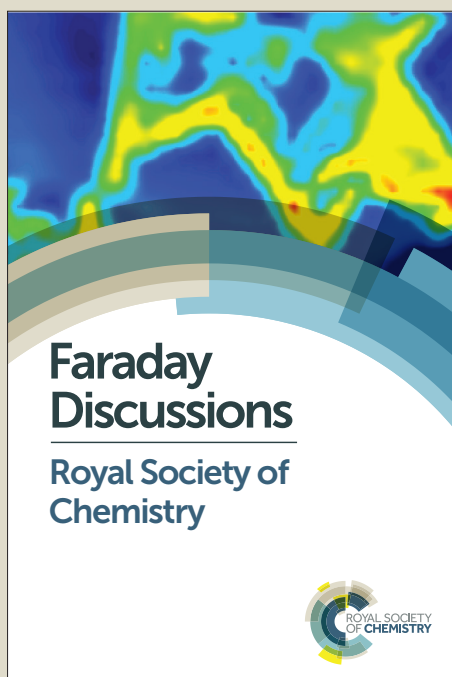
# Faraday Discussions

Accepted Manuscript



This manuscript will be presented and discussed at a forthcoming Faraday Discussion meeting. All delegates can contribute to the discussion which will be included in the final volume.

**Register now to attend!** Full details of all upcoming meetings: <http://rsc.li/fd-upcoming-meetings>



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

## Concluding Remarks: There's Nowt so Queer as Carbon Electrodes

Patrick Unwin\*

DOI: 10.1039/b000000x [DO NOT ALTER/DELETE THIS TEXT]

5 I would like to thank Katherine [Holt] for inviting me to give the 'Concluding Remarks' at this *Faraday Discussion*. I was delighted to accept, not only because I have considerable interest in carbon electrodes, but also - as a proud Yorkshireman - it's always wonderful to come home to 'God's own County' (even, as a Leeds lad, to Sheffield)! I do have to warn you, however, that Yorkshire folk (or 'Tykes' as we are 'affectionately' known) are often stereotyped as "*friendly, but bloody-minded and argumentative*"; and that's according to Wikipedia,<sup>1</sup> so it must be true! On reflection, that may be the perfect  
10 attribute to participate in a *Faraday Discussion* on "*Carbon in Electrochemistry*" and give these particular 'Remarks'. As this has been a most interesting, but at times serious and intense, meeting, I aim to lighten the mood a little. Prepare for Yorkshire (and Sheffield) references to be sprinkled liberally! Indeed, as we have discussed spatial heterogeneity extensively, let's set the scene with an appreciation of the beautiful characteristic topography of the world-famous Yorkshire Dales (Figure 1).

15



Figure 1. Early spring in Upper Swaledale, North Yorkshire.

20 We were naturally very pleased in the Warwick Electrochemistry & Interfaces Group that the Faraday Division of the RSC chose to use one of our images for the publicity and announcements for this *Discussion* (Figure 2 and elsewhere<sup>2</sup>). This picture is not a map of some far off world or a distorted view of our own planet! Rather, it's data showing the electrochemical activity of a polycrystalline diamond electrode, which evidently varies spatially.<sup>3</sup> On a different scale the surface of a diamond electrode, topographically, is not unlike the beautiful Limestone Pavement in Malham Cove, North  
25 Yorkshire, comprising facets and grain boundaries. This type of heterogeneity goes to the heart of many of the issues we have addressed in this meeting: carbon electrode surfaces often comprise such features and other defects, and this may impact massively on the electrochemical properties that have been considered extensively in this *Discussion*. The challenge is to be able to identify and characterise these surface features and demonstrate unambiguously how they influence electrochemical reactions.

30

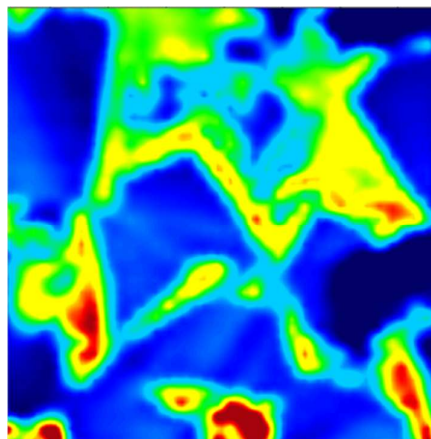


Figure 2. Electrochemical map of a polycrystalline diamond electrode, adapted for the publicity graphic for this *Discussion* (e.g. as featured on the front cover of this volume<sup>2</sup>).

### Local character

Sheffield is a particularly appropriate location for this meeting on ‘carbon’, because we are situated here above the great South Yorkshire Coalfield, with coal mining in this area stretching back to Roman times, until Margaret Thatcher put a stop to it! And, of course, the city of Sheffield is world famous for cutlery manufacture, with a long history, as far back as the late 13<sup>th</sup> century, and a mention in Chaucer’s *Canterbury Tales*.<sup>4</sup> Crucible steel was manufactured extensively in this region during the Industrial Revolution, and stainless steel was discovered in Sheffield by Harry Brearley just over 100 years ago. In one of the papers on supercapacitors,<sup>5</sup> we heard about steel working electrodes. So, there really is nowhere better than Yorkshire, and Sheffield, to have this meeting.

Yorkshire is famous for many unique and distinctive phrases, and I have drawn on one, ‘There’s nowt so queer as folk’ or, to translate, ‘There’s nothing so peculiar as people’ as the title for this talk. Why do I consider this appropriate? Well, as evident in some of the papers and debate in this meeting, and in work elsewhere,<sup>6-13</sup> carbon electrodes really do seem to have the most peculiar behaviour, with apparently the same material in different labs (and sometimes in different eras) giving rather different results. A major challenge in the field is to understand and rationalise these differences. For the present, it has proven difficult to pin down the electrochemical behaviour of related new forms of carbon, such as graphene. Thus, is graphene more<sup>14, 15</sup> or less<sup>16</sup> active than graphite, even for very simple outer sphere electron transfer processes? Similarly, for outer sphere redox couples, we may look at work in the field and ask are single walled carbon nanotubes (SWNTs) only active at their ends,<sup>17-19</sup> and do such ends have to be open and oxygen functionalised?<sup>18, 19</sup> Or do SWNTs have intrinsic activity on the sidewall?<sup>20-24</sup> We have had several papers on polycrystalline diamond electrodes, with applications spanning electroanalysis, electrocatalysis and electrodeposition. Yet, outside this meeting, there has been considerable debate on the active sites for electrochemistry at polycrystalline diamond, with high resolution electrochemical imaging providing insights into structural controls of electrochemical activity that are important for both fundamental understanding of charge transfer at this material,<sup>3</sup> and optimised applications. Although progress is being made in relating structure (and other surface properties) to activity, there is a long way to go, so with apologies for the anthropomorphism, and to the *Arctic Monkeys*, if carbon electrodes could speak they would probably say, for the moment, “*Whatever people say I am, that’s what I’m not*”. And, for those not into English indie rock, that was another Sheffield reference!

### Reviewing the rationale

A wide range of studies has been presented at this meeting attempting to address the electroactivity of carbon electrodes at different length scales and under a diversity of conditions. Thus, we heard about the electrodeposition and stripping of carbon at high temperature, from George Chen,<sup>25</sup> and, on the other hand, the modification of graphene around point defects from Keith Stevenson<sup>26</sup> (a study I will mention again later). This *Discussion* has been very successful in highlighting the wide variety of studies that constitutes the use of carbon in electrochemistry.

In setting up the *Discussion*, the Scientific Committee outlined 4 points as a rationale, and it is useful to look at each in turn, in light of the papers presented. The first point was that “*Carbon is ubiquitous in electrochemical research....*” and we have certainly seen that in this meeting, which has been very successful in covering a wide range of topics in considerable depth. There is evidently much interest in the use of carbon electrodes in batteries,<sup>27, 28</sup> and three papers in the session on supercapacitors<sup>5, 29, 30</sup> generated a huge amount of discussion and debate that could have gone on for much longer had the tea/coffee break not been called! There is clearly a lot of exciting work, and some controversy, in that area, and many new materials and concepts are coming through. The topic of electrochemical biosensors, likewise, was wide-ranging, from implant electrodes based on diamond microelectrode arrays<sup>31</sup> to the detection of biomolecules in solution,<sup>32</sup> and attempts to understand coupled electron transfer-proton transfer reactions, and the influence of electrode structure on such processes. Key properties of carbon electrodes that have come up in many of the discussions have been electrical conductivity, chemical functionality and biocompatibility. We even had a debate on the first afternoon about economics and carbon

trading!

The second point was “...the use of carbon in more novel forms (e.g. carbon nanotubes, graphene) has impacted on all areas of fundamental and applied electrochemistry...” In this respect, we have certainly covered many more types of carbon than I envisaged. One would have predicted that graphene,<sup>26, 32-34</sup> highly oriented pyrolytic graphite (HOPG),<sup>35</sup> nanotubes,<sup>36</sup> glassy carbon<sup>37</sup> and diamond<sup>31, 38-40</sup> would feature prominently, but we have also heard about nanoflakes,<sup>34</sup> nanodiamond,<sup>39</sup> a lot on carbon composites,<sup>27, 41-43</sup> support effects<sup>32, 43</sup> and porous materials.<sup>30</sup> This diversity and complexity in the types of carbon materials found in electrochemistry raises challenges as to how to look at these materials. This brings us to the third point which was “Advanced electrochemical techniques such as scanning electrochemical microscopy, electrochemical AFM and spectroelectrochemistry have moreover increased our understanding of the interfacial properties of traditional carbon electrode materials”. This is certainly true, as these techniques allow access to structure-function directly and simultaneously,<sup>6, 7, 44-48</sup> as highlighted above, and they can provide insight into chemical speciation during electrochemical reactions at carbon electrodes.<sup>49, 50</sup> However, these types of methodologies did not feature as prominently in this *Discussion* as I expected, although they were evident.<sup>26, 36</sup> Such approaches, and others, have an important role to play in the future, and I will return to this shortly.

The final aspect was that “Carbon also plays an important role in technologically applied areas of electrochemistry - in energy generation and storage and catalyst support”. This issue was covered admirably, for example, with sub-nanoporous carbide-derived carbons<sup>30</sup> and multi-functional structural composites for energy storage,<sup>42</sup> where the importance not only of electrochemical performance, but also structural integrity was highlighted. We also heard about the use of redox active electrolytes for supercapacitors.<sup>29</sup> But, I think, the technological highlight was undoubtedly Rick’s [McCreery] amazing ‘electrochemical guitar pedal’, based on an innovative carbon-based molecular junction and showcased with audio in the *Introductory Lecture*.<sup>35</sup> There is a future for this! Perhaps the hard-rocking Sheffield band, Def Leopard, might be interested? As Rick got this *Discussion* off to a musical start, I am happy to conclude in similar fashion!

### Macroscopic to microscopic

An enduring theme of this meeting is that many papers tended to focus on average properties and we had a lot of current-voltage curves! As electrochemists, we know that current-voltage relationships have their place, but considerable care is needed when developing microscopic models from such measurements. We still rely heavily on correlations in electrochemistry, and particularly in studies of carbon electrodes, because (traditionally) they have been difficult to characterise microscopically, but it is important to bear in mind that just because one quantity appears to correlate with another does not mean there is necessarily a physical relationship between the two. Models derived in this way need to be tested continuously with new, emerging microscopic techniques. The electrochemical response of simple redox couples, notably  $\text{Fe}(\text{CN})_6^{4-/3-}$ , has become a proxy for the surface quality (defect concentration) of graphitic materials and carbon nanotubes,<sup>13, 19, 51-53</sup> and is now widely used in that context,<sup>54-58</sup> but there are many other issues that can impact the response of (layered) carbon electrodes, such as the adsorption of adventitious material (impurities),<sup>6, 59, 60</sup> delamination,<sup>6, 61</sup> surface oxidation, etc. So, without careful control of these parameters, macroscopic CV measurements, where one simply looks for ‘sluggish kinetics’ as an indicator of ‘quality’, do not provide an unambiguous view of (high) surface quality. Indeed, although  $\text{Fe}(\text{CN})_6^{4-/3-}$  was used as the main method to ‘select’ particular HOPG surfaces for further study in earlier work,<sup>13, 51, 52</sup> it is not a straightforward couple even on well-defined and easily prepared metal electrodes,<sup>62, 63</sup> and recent work highlights complicated factors in its study at graphite (HOPG) electrodes.<sup>6</sup> Without a detailed understanding of structural controls of apparently simple electron transfer processes at well-defined graphitic electrodes, it will be difficult for the field to advance to understand more complex reactions and carbon materials. This situation contrasts markedly to the studies of precious metal electrodes, for example, platinum, where CV measurements can give considerable information on the structure and status of the electrode.<sup>64-66</sup> Challenges for the study of carbon electrodes would be: to identify similar unambiguous CV signatures indicative of surface quality; to make more widespread use of high resolution structural techniques to characterise materials used for electrochemistry, as highlighted in several papers in this *Discussion*; and to make more use of microscopic and nanoscopic electrochemical probes where one can target particular surface features of interest.

Capacitance measurements also featured strongly at the macroscopic level, along with related measurements such as the determination of active surface area from redox probe adsorption and gas adsorption.<sup>30, 37, 43</sup> There were interesting questions and debate about the limitations of these approaches. The importance of nanoscale properties featured a lot in the discussions, but there was a tendency to talk in very general terms about defects or dangling bonds, and much more needs to be known about these issues. We also need more dialogue between different groups about surface quality, functionality, reproducibility. We had some contributions to the debate along the lines that really nice super-clean, low defect graphene can be made very easily by chemical vapour deposition, whereas other groups recognise that there are many issues to making (and retaining) such materials with high surface purity. Which is correct?

### ‘The Full Monty’

So how do we move forward to improve our understanding? To begin with, I believe we have to focus on well-defined planar carbon surfaces (e.g. well-defined HOPG and conducting single crystal diamond), as these materials can now be characterised fairly easily in a variety of ways. But we have to ensure the surfaces are as close to pristine as possible. Individual point defects can be characterised with STM, as Keith Stevenson showed in this meeting for graphene.<sup>26</sup> Others have shown for HOPG that such defects are of low concentration and in a narrow range of  $0.1 - 10 \mu\text{m}^{-2}$ .<sup>67-69</sup> In fact, a recent

high resolution STM study of HOPG surface modification failed to find a single point defect in over 100 images (typically 25 nm<sup>2</sup> area per image).<sup>70</sup> Thus, we should be able to pin down the importance (or otherwise) of such features). Step edges, which are the main ‘defect site’ on such surfaces, are routinely quantified with AFM.<sup>6, 7, 10, 47</sup> Thus studying different grades of HOPG (see for example Figure 3A) even by macroscopic electrochemistry opens up the possibility of determining how step edge density impacts (or otherwise) various electrochemical processes.<sup>10, 71</sup>

Well-characterised nanomaterials are now also amenable to study, such as single layer graphene, graphene bilayers, multiple layers, individual edges, and nanotubes. This meeting,<sup>36</sup> and related work,<sup>23, 72</sup> has shown that it is now possible to understand multiple properties of an individual SWNT and relate these to the electrochemistry. Although challenging experimentally, defects in SWNTs can also be visualised with a range of techniques,<sup>23, 73-75</sup> and it should thus be possible to assess the impact of defects on electrochemistry with high resolution electrochemical microscopy.

It is evidently important to understand the local electronic structure of carbon materials, and this was raised several times in the *Discussion*. Scanning tunnelling spectroscopy (STS) studies are revealing considerable information about the local density of states (LDOS) of various carbon materials.<sup>61, 76</sup> For HOPG, a major outcome is that the LDOS is similar at armchair edges as at the basal surface away from the edge, and only enhanced at zigzag edges, which are the minority edge (see Figure 3B). Thus, unless the density of such edges is very high (< 10 nm spacing), the overall DOS at HOPG is essentially constant across the different grades of HOPG.<sup>77</sup> This is significant because it opens up the possibility - even on the macroscopic scale - of separating DOS effects from step edge density effects (and other defect effects, assuming that point defects, and other electronic disturbances that may occur in the basal surface<sup>61, 78-80</sup> remain unimportant or can be quantified). Thus, for HOPG, and other carbon materials, it should be possible to build a very detailed picture of activity, by combining sophisticated surface structure probes and electrochemical measurements, while also taking precautions to avoid surface contamination.

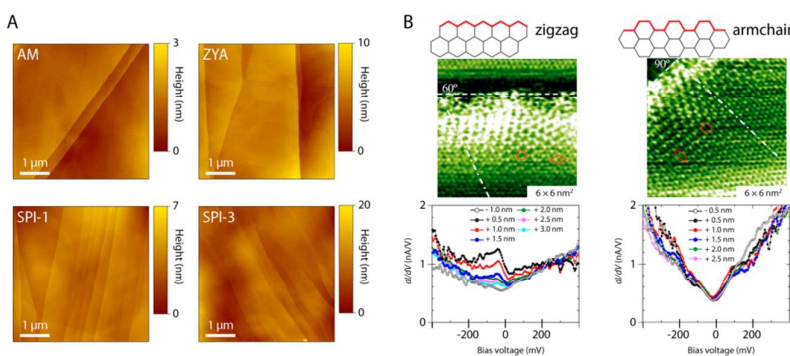


Figure 3. (A) AFM images of different grades of HOPG (note the different height scales). (B) STM images of HOPG near a monoatomic step edge for zigzag (left) and armchair (right) edges. The dI/dV curves were measured at difference distances from the edge. Adapted with permission from references 10 and 77.

So, in essence, I am arguing that to move the field forward we need the ‘Full Monty’! The title of this Great British film about 5 unemployed guys from Sheffield who form a striptease act most likely has its origin in the ‘full Montague Burton (3-piece) suit’ (from Leeds), and basically means ‘everything’ or ‘the full works’. So who are the ‘Full Monty electrochemists’ at this *Discussion*? First, Keith [Stevenson] showed us how STM measurements revealed the importance of defects vs. basal activity during the functionalization of graphene.<sup>26</sup> Rob [Dryfe] tackled the issue of environment/impurity effect on graphene electroactivity, and used a microdroplet to probe a single layer, two layers, etc., unambiguously, with knowledge of the environment of the graphene surface and how that impacted electrochemistry. Lawrence [Hardwick] told us about making *in-situ* Raman measurements at micro-graphite electrodes during lithium intercalation and de-intercalation, with major implications for understanding the functioning of lithium ion batteries. This was a distinctive contribution, because while Raman spectroscopy is a natural complement to electrochemistry to enable understanding of the structure and properties of carbon,<sup>81, 82</sup> and was mentioned a great deal at this meeting, *in-situ* work has been rare. Alex [Güell], described a multi-technique platform, where many techniques, including high resolution electrochemical imaging can be applied to individual nanomaterials.<sup>36</sup> A word of advice though guys – stick to the electrochemistry!

Outside of this meeting, there is evidence that other groups are embracing this philosophy. So Phil Collins’ group (University of California, Irvine) has recently investigated the charge transfer resistance of individual SWNT composites.<sup>83</sup> This is a particularly nice study because it contributes to fundamental understanding of heterogeneous electron transfer, making use of individual pristine carbon nanotubes coated with a metal-oxide electrochemical-storage material. The experiments rule out any significant role of SWNT defects or band structure in the electrochemistry of this kind of composite. Moreover, the results contradict the expectation of enhanced out-of-plane electron transfer rates from defective (step edge) sp<sup>2</sup> carbon, based on older HOPG literature.<sup>8, 9, 11, 12, 51, 52, 84</sup> These studies found that multi-walled carbon nanotubes, platinum, HOPG and SWNTs had essentially the same charge transfer characteristics, even though they have very different electronic band structure. These kinds of studies are essential to challenge preconceptions and promote progress in this field.

## Back to Yorkshire

As a beneficiary of an enlightened education environment in West Yorkshire in the early 1970's, under Sir Alec Clegg, I would like to close by quoting from an after dinner speech he gave at a workshop for school teachers in Bingley, West Yorkshire, just over 40 years ago. Entitled "Making the whole world wonder",<sup>85</sup> his speech is illuminating and I encourage you to read it. In part of the speech he identified the characteristics he had seen in the greatest teachers (and by extension, I believe, these attributes make the best researchers):

"They were immersed in - and constantly excited by - what they were doing. They were innovators. They modified their views continuously as they learned from their experiences...and from the ideas that they picked up outside and wished to try out. Their professional life was a creative quest."

While we (and the public) often link science with innovation and excitement, it can - at the same time - be very conservative, and hierarchical. Ideas can become entrenched (and personal), and the history of science tells us that change can be a painful, long and difficult process. Yet, science is not set in stone, and this is particularly true of electrochemistry. The challenge of studying complex electrochemical interfaces means that our views will change continuously, as new techniques and methods become available. This meeting has highlighted the tremendous potential of carbon materials for both fundamental and applied studies in electrochemistry, but we have much to learn, and our views will change. Carbon electrodes may have been around for a long time in electrochemistry, but this *Discussion* has highlighted that we are entering a new era of understanding.

I hope you have enjoyed your time in Yorkshire and this *Discussion* on "Carbon in electrochemistry".

## Acknowledgements

I would like to acknowledge many colleagues at Warwick with whom I have had interesting and illuminating discussions on carbon electrodes. I am particularly grateful to the electrochemical imaging team who have brought many new perspectives to bear on the local electrochemistry of carbon electrodes, aided by generous support from the European Research Council (ERC-2009-AdG247143-QUANTIF). I would like to thank Aleix Güell and Guohui Zhang for their help and advice in the preparation of this manuscript.

## References

\* Department of Chemistry, University of Warwick, Coventry CV4 7AL, United Kingdom. Fax: +44 (0)2476 524112; Tel: +44 (0) 2476 523264; E-mail: p.r.unwin@warwick.ac.uk

1. [http://en.wikipedia.org/wiki/Culture\\_of\\_Yorkshire](http://en.wikipedia.org/wiki/Culture_of_Yorkshire). (Accessed on 5 October 2014)
2. <http://www.rsc.org/conferencesandevents/rscconferences/fd/fd172/index.asp>. (Accessed on 5 October 2014)
3. H. V. Patten, K. E. Meadows, L. A. Hutton, J. G. Iacobini, D. Battistel, K. McKelvey, A. W. Colburn, M. E. Newton, J. V. Macpherson and P. R. Unwin, *Angew. Chem. Int. Ed.*, 2012, **51**, 7002-7006.
4. G. Chaucer, in *The Canterbury Tales*. The Reeve's Tale. 'Ther was no man, for peril, dorste hym touche. A Sheffeld thwitel baar he in his hose. Round was his face, and camus was his nose'.
5. Q. Abbas, P. Ratajczak and F. Beguin, *Faraday Discuss.*, 2014, DOI: 10.1039/C4FD00056K.
6. A. N. Patel, M. G. Collignon, M. A. O'Connell, W. O. Hung, K. McKelvey, J. V. Macpherson and P. R. Unwin, *J. Am. Chem. Soc.*, 2012, **134**, 20117-20130.
7. S. C. S. Lai, A. N. Patel, K. McKelvey and P. R. Unwin, *Angew. Chem. Int. Ed.*, 2012, **51**, 5405-5408.
8. T. J. Davies, M. E. Hyde and R. G. Compton, *Angew. Chem. Int. Ed.*, 2005, **44**, 5121-5126.
9. C. E. Banks, T. J. Davies, G. G. Wildgoose and R. G. Compton, *Chem. Commun.*, 2005, 829-841.
10. G. Zhang, P. M. Kirkman, A. N. Patel, A. S. Cuharuc, K. McKelvey and P. R. Unwin, *J. Am. Chem. Soc.*, 2014, **136**, 11444-11451.
11. M. T. McDermott and R. L. McCreery, *Langmuir*, 1994, **10**, 4307-4314.
12. M. T. McDermott, K. Kneten and R. L. McCreery, *J. Phys. Chem.*, 1992, **96**, 3124-3130.
13. K. R. Kneten and R. L. McCreery, *Anal. Chem.*, 1992, **64**, 2518-2524.
14. W. Li, C. Tan, M. A. Lowe, H. D. Abruña and D. C. Ralph, *ACS Nano*, 2011, **5**, 2264-2270.
15. A. T. Valota, I. A. Kinloch, K. S. Novoselov, C. Casiraghi, A. Eckmann, E. W. Hill and R. A. W. Dryfe, *ACS Nano*, 2011, **5**, 8809-8815.
16. A. G. Güell, N. Ebejer, M. E. Snowden, J. V. Macpherson and P. R. Unwin, *J. Am. Chem. Soc.*, 2012, **134**, 7258-7261.
17. J. J. Gooding, R. Wibowo, Liu, W. Yang, D. Losic, S. Orbons, F. J. Mearns, J. G. Shapter and D. B. Hibbert, *J. Am. Chem. Soc.*, 2003, **125**, 9006-9007.
18. A. Chou, T. Bocking, N. K. Singh and J. J. Gooding, *Chem. Commun.*, 2005, 842-844.
19. A. F. Holloway, K. Toghiani, G. G. Wildgoose, R. G. Compton, M. A. H. Ward, G. Tobias, S. A. Llewellyn, B. Ballesteros, M. L. H. Green and A. Crossley, *J. Phys. Chem. C*, 2008, **112**, 10389-10397.
20. I. Heller, J. Kong, H. A. Heering, K. A. Williams, S. G. Lemay and C. Dekker, *Nano Lett.*, 2004, **5**, 137-142.
21. A. G. Güell, N. Ebejer, M. E. Snowden, K. McKelvey, J. V. Macpherson and P. R. Unwin, *Proc. Natl. Acad. Sci. U. S. A.*, 2012, **109**, 11487-11492.
22. A. G. Güell, K. E. Meadows, P. V. Dudin, N. Ebejer, J. V. Macpherson and P. R. Unwin, *Nano Lett.*, 2014, **14**, 220-224.
23. J. C. Byers, A. G. Güell and P. R. Unwin, *J. Am. Chem. Soc.*, 2014, **136**, 11252-11255.
24. T. S. Miller, N. Ebejer, A. G. Güell, J. V. Macpherson and P. R. Unwin, *Chem. Commun.*, 2012, **48**, 7435-7437.
25. H. V. Ijije, R. C. Lawrence, N. J. Siambun, S. M. Jeong, D. A. Jewell, D. Hu and G. Z. Chen, *Faraday Discuss.*, 2014, DOI: 10.1039/C4FD00046C.
26. K. J. V. Stevenson, P. A.: Gearba, R. I.; Mueller, K. M.; Holliday, B. J.; Ohta, T.; Chan, C. K., *Faraday Discuss.*, 2014, DOI: 10.1039/C4FD00038B.
27. Y. Cao, S.-R. Cai, S.-C. Fan, W.-Q. Hu, M.-S. Zheng and Q.-F. Dong, *Faraday Discuss.*, 2014, DOI: 10.1039/C4FD00075G.
28. C. Sole, N. E. Drewett and L. J. Hardwick, *Faraday Discuss.*, 2014, DOI: 10.1039/C4FD00079J.
29. E. Frackowiak, M. Meller, J. Menzel, D. Gastol and K. Fic, *Faraday Discuss.*, 2014, DOI: 10.1039/C4FD00052H.
30. B. Dyatkin and Y. Gogotsi, *Faraday Discuss.*, 2014, DOI: 10.1039/C4FD00048J.

31. C. Hebert, E. Scorsone, A. Bendali, R. Kiran, M. Cottance, H. A. Girard, J. Degardin, E. Dubus, G. Lissorgues, L. Rousseau, P. Mailley, S. Picaud and P. Bergonzo, *Faraday Discuss.*, 2014, DOI: 10.1039/C4FD00040D.
32. J. Hu, S. Wisetsuwannaphum and J. S. Foord, *Faraday Discuss.*, 2014, DOI: 10.1039/C4FD00032C.
33. N. L. Ritzert, W. Li, C. Tan, G. G. Rodriguez-Calero, J. Rodriguez-Lopez, K. Hernandez-Burgos, S. Conte, J. J. Parks, D. C. Ralph and H. D. Abruna, *Faraday Discuss.*, 2014, DOI: 10.1039/C4FD00060A.
34. M. M. Lounasvuori, M. Rosillo-Lopez, C. G. Salzmann, D. J. Caruana and K. B. Holt, *Faraday Discuss.*, 2014, DOI: 10.1039/C4FD00034J.
35. R. McCreery, A. Bergren, A. Morteza-Najarian, S. Nagy and H. Yan, *Faraday Discuss.*, 2014, DOI: 10.1039/C4FD00172A.
36. A. G. Güell, K. E. Meadows, P. V. Dudin, N. Ebejer, J. C. Byers, J. V. Macpherson and P. R. Unwin, *Faraday Discuss.*, 2014, DOI: 10.1039/C4FD00054D.
37. A. Noofeli, P. J. Hall and A. J. R. Rennie, *Faraday Discuss.*, 2014, DOI: 10.1039/C4FD00057A.
38. L. Meng, J. G. Jacobini, M. B. Joseph, J. V. Macpherson and M. E. Newton, *Faraday Discuss.*, 2014, DOI: 10.1039/C4FD00044G.
39. T. S. Varley, M. Hirani, G. Harrison and K. B. Holt, *Faraday Discuss.*, 2014, DOI: 10.1039/C4FD00041B.
40. R. Hamers, J. N. Bandy, L. Zhang and D. Zhu, *Faraday Discuss.*, 2014, DOI: 10.1039/C4FD00039K.
41. S. A. Hodge, H. H. Tay, D. B. Anthony, R. Menzel, D. J. Buckley, P. L. Cullen, N. T. Skipper, C. A. Howard and M. S. P. Shaffer, *Faraday Discuss.*, 2014, DOI: 10.1039/C4FD00043A.
42. N. Shirshova, H. Qian, M. Houille, J. H. G. Steinke, A. R. J. Kucernak, Q. P. V. Fontana, E. S. Greenhalgh, A. Bismarck and M. S. P. Shaffer, *Faraday Discuss.*, 2014, DOI: 10.1039/C4FD00055B.
43. J. Quinson, R. Hidalgo, P. A. Ash, F. Dillon, N. Grobert and K. A. Vincent, *Faraday Discuss.*, 2014, DOI: 10.1039/C4FD00058G.
44. N. Ebejer, A. G. Güell, S. C. S. Lai, K. McKelvey, M. E. Snowden and P. R. Unwin, *Annu. Rev. Anal. Chem.*, 2013, **6**, 329-351.
45. N. Ebejer, M. Schnippering, A. W. Colburn, M. A. Edwards and P. R. Unwin, *Anal. Chem.*, 2010, **82**, 9141-9145.
46. P. L. Frederix, P. D. Bosshart, T. Akiyama, M. Chami, M. R. Gullo, J. J. Blackstock, K. Dooleweerd, N. F. de Rooij, U. Staufer and A. Engel, *Nanotechnology*, 2008, **19**, 384004.
47. A. N. Patel, S. Y. Tan, T. S. Miller, J. V. Macpherson and P. R. Unwin, *Anal. Chem.*, 2013, **85**, 11755-11764.
48. A. J. Wain, A. J. Pollard and C. Richter, *Anal. Chem.*, 2014, **86**, 5143-5149.
49. N. González-Diéguez, A. Colina, J. López-Palacios and A. Heras, *Anal. Chem.*, 2012, **84**, 9146-9153.
50. J. Garoz-Ruiz, D. Izquierdo, A. Colina, S. Palmero and A. Heras, *Anal. Bioanal. Chem.*, 2013, **405**, 3593-3602.
51. R. J. Rice and R. L. McCreery, *Anal. Chem.*, 1989, **61**, 1637-1641.
52. K. K. Cline, M. T. McCreery and R. L. McCreery, *J. Phys. Chem.*, 1994, **98**, 5314-5319.
53. C. E. Banks, R. R. Moore, T. J. Davies and R. G. Compton, *Chem. Commun.*, 2004, DOI: 10.1039/B406174H, 1804-1805.
54. M. Pumera, *Electrochem. Commun.*, 2013, **36**, 14-18.
55. A. Ambrosi, C. K. Chua, A. Bonanni and M. Pumera, *Chem. Rev.*, 2014, **114**, 7150-7188.
56. D. K. Kampouris and C. E. Banks, *Chem. Commun.*, 2010, **46**, 8986-8988.
57. D. A. C. Brownson, D. K. Kampouris and C. E. Banks, *Chem. Soc. Rev.*, 2012, **41**, 6944-6976.
58. S. Palanisamy, R. Madhu, S.-M. Chen and S. K. Ramaraj, *Anal. Methods*, 2014, **6**, 8368-8373.
59. Z. Li, Y. Wang, A. Kozbial, G. Shenoy, F. Zhou, R. McGinley, P. Ireland, B. Morganstein, A. Kunkel, S. P. Surwade, L. Li and H. Liu, *Nat. Mater.*, 2013, **12**, 925-931.
60. A. Kozbial, Z. Li, J. Sun, X. Gong, F. Zhou, Y. Wang, H. Xu, H. Liu and L. Li, *Carbon*, 2014, **74**, 218-225.
61. G. Li, A. Luican and E. Y. Andrei, *Phys. Rev. Lett.*, 2009, **102**, 176804.
62. C. M. Pharr and P. R. Griffiths, *Anal. Chem.*, 1997, **69**, 4673-4679.
63. J. López-Palacios, A. Heras, Á. Colina and V. Ruiz, *Electrochim. Acta*, 2004, **49**, 1027-1033.
64. J. Mostany, E. Herrero, J. M. Feliu and J. Lipkowsky, *J. Phys. Chem. B*, 2002, **106**, 12787-12796.
65. N. Garcia-Araez, V. Climent and J. Feliu, *J. Phys. Chem. C*, 2009, **113**, 9290-9304.
66. V. Climent and J. Feliu, *J. Solid State Electrochem.*, 2011, **15**, 1297-1315.
67. H. Chang and A. J. Bard, *J. Am. Chem. Soc.*, 1991, **113**, 5588-5596.
68. H. Chang and A. J. Bard, *J. Am. Chem. Soc.*, 1990, **112**, 4598-4599.
69. J. V. Zoval, R. M. Stiger, P. R. Biernacki and R. M. Penner, *J. Phys. Chem.*, 1996, **100**, 837-844.
70. H. Ma, L. Lee, P. A. Brooksby, S. A. Brown, S. J. Fraser, K. C. Gordon, Y. R. Leroux, P. Hapiot and A. J. Downard, *J. Phys. Chem. C*, 2014, **118**, 5820-5826.
71. A. N. Patel, S. Y. Tan and P. R. Unwin, *Chem. Commun.*, 2013, **49**, 8776-8778.
72. P. V. Dudin, M. E. Snowden, J. V. Macpherson and P. R. Unwin, *ACS Nano*, 2011, **5**, 10017-10025.
73. K. Suenaga, H. Wakabayashi, M. Koshino, Y. Sato, K. Urita and S. Iijima, *Nat. Nano.*, 2007, **2**, 358-360.
74. Z. Osváth, G. Vértsey, L. Tapasztó, F. Wéber, Z. E. Horváth, J. Gyulai and L. P. Biró, *Phys. Rev. B*, 2005, **72**, 045429.
75. Y. Fan, B. R. Goldsmith and P. G. Collins, *Nat. Mater.*, 2005, **4**, 906-911.
76. W. O. Teri, H. Jin-Lin and M. L. Charles, *J. Phys.: Condens. Matter*, 2002, **14**, R145.
77. Y. Niimi, T. Matsui, H. Kambara, K. Tagami, M. Tsukada and H. Fukuyama, *Phys. Rev. B*, 2006, **73**, 085421.
78. A. Luican, G. Li and E. Y. Andrei, *Solid State Commun.*, 2009, **149**, 1151-1156.
79. Y. A. Eva, L. Guohong and D. Xu, *Rep. Prog. Phys.*, 2012, **75**, 056501.
80. G. Li, A. Luican, J. M. B. Lopes dos Santos, A. H. Castro Neto, A. Reina, J. Kong and E. Y. Andrei, *Nat. Phys.*, 2010, **6**, 109-113.
81. Y. Wang, D. C. Alsmeyer and R. L. McCreery, *Chem. Mater.*, 1990, **2**, 557-563.
82. M. S. Dresselhaus, A. Jorio and R. Saito, *Annu. Rev. Condens. Matter Phys.*, 2010, **1**, 89-108.
83. B. L. Corso, I. Perez, T. Sheps, P. C. Sims, O. T. Gül and P. G. Collins, *Nano Lett.*, 2014, **14**, 1329-1336.
84. R. J. Bowling, R. T. Packard and R. L. McCreery, *J. Am. Chem. Soc.*, 1989, **111**, 1217-1223.
85. <http://www.educationengland.org.uk/documents/speeches/1972clegg.html>. (Accessed on 5 October 2014)

65