

## Carbon electrodes for energy storage: general discussion

Yury Gogotsi, Dirk Guldi, Richard McCreery, Chi-Chang Hu, Céline Merlet, François Béguin, Laurence Hardwick, Elzbieta Frackowiak, Julie Macpherson, Alexander Forse, George Zheng Chen, Katherine Holt, Robert Dryfe, Heisi Kurig, Surbhi Sharma, Patrick R. Unwin, Thomas Rabbow, Wanjing Yu, Fulian Qiu, Fernanda Juarez, Christopher Sole, Boris Dyatkin, Keith Stevenson, Yong Cao, Nico Cousens and Asa Noofeli

DOI: 10.1039/C4FD90026J

**François Béguin** opened the discussion of the paper by Yury Gogotsi: After vacuum treatment of the SiC-CDC at 700 °C, the specific surface area increases by around 1000 m<sup>2</sup> g<sup>-1</sup>. You explain it by the removal of surface functional groups. However, the elemental analysis in table 1 shows almost the same composition for the initial CDC and 700 °C annealed. How can you explain such a high increase of surface area without any change of elemental composition?

**Yury Gogotsi** answered: We assume that the SSA increase is due to desorption of surface functional groups that take carbon atoms along.<sup>1</sup> However, adsorption of water, CO<sub>2</sub> and other species from the environment leads to increased oxygen content in the samples shown by X-ray energy dispersive spectroscopy.

1 B.J.M. Etzold *et al.*, *Chem. Mat.*, 2014, 26, 3479–3484.

**François Béguin** continued: Thermal treatments of carbons either under neutral gas or under vacuum allow the removal of surface functional groups. However, they require a further ‘passivation’ of the surface, *e.g.* by dihydrogen, to neutralize the free radicals, often called dangling bonds. If not, the free radicals may lead to electrolyte decomposition, reducing the voltage window of the system.

**Yury Gogotsi** replied: I agree. We should do hydrogen treatment after vacuum annealing, in the same way as we do it after CDC synthesis.

**Chi-Chang Hu** asked: For the electrolytes containing large cations and anions, is the charge storage mechanism of carbide-derived carbons with sub-nanometer pores more reasonably attributed to an intercalation/de-intercalation process or

specific adsorption of ions? How does the pore depth affect the charge storage/delivery rate?

**Yury Gogotsi** responded: I would call it electrosorption rather than intercalation. However, when the pore size is close to the ion size, expansion of the electrodes occurs<sup>1</sup> with the ion insertion process becoming similar to intercalation. The pore depth, as determined by the particle size or film thickness, controls the power to a large extent. However, above a certain critical pore length, the electrode cannot be fully charged and its capacitance becomes limited by the pore length, because some inner pores cannot be accessed by ions.<sup>2</sup>

1 M. M. Hantel *et al.*, *Electrochem. Comm.*, 2011, **13**, 1221–1224.

2 J. Chmiola *et al.*, *Science*, 2010, **328**, 480–483.

**François Béguin** remarked: One delegate suggested that ions could be intercalated. Pure intercalation would require an electron transfer. In other words, in EDLC based on porous carbon electrodes, it is considered that ions are purely electrosorbed. However, with some carbons, Koetz experiments demonstrated volume expansion of around 10%. Such high values suggest some constrained state of ions in narrow pores.

**Yury Gogotsi** answered: This is correct. We observed up to ~5% expansion for CDC.<sup>1</sup>

1 M. M. Hantel *et al.*, *Electrochem. Comm.*, 2011, **13**, 1221–1224.

**Elzbieta Frackowiak** enquired: Do you think that the pores of CDC carbons could be closed during heat treatment at temperatures over 1050 °C ? Such a phenomenon is very well known for various carbonaceous materials.

**Yury Gogotsi** replied: This depends on the carbon structure. During the CDC synthesis, graphitic ordering is seen above 1100 °C. CDCs produced at low temperatures (200–600 °C) can be restructured at temperatures below 1000 °C, but no structure collapse happens in most CDCs during annealing in vacuum up to about 1500 °C. They have a 3D covalent network, which is very stable, as it requires bond breaking for restructuring. Pore collapse and decrease in SSA happen at 1600 °C and above.

**George Zheng Chen** asked: What may be the reason for the different capacitance values of your carbon samples, apart from the pore sizes?

**Yury Gogotsi** answered: Surface chemistry and carbon structure (ordering), which determine the quantum capacitance, affect the electrode capacitance values at a given pore size.

**Céline Merlet** addressed Yury Gogotsi and George Zheng Chen: The models used in molecular simulations do not currently take into account the functionalities or defects present at the carbon surface in real systems. In simulations, the carbon is treated as a metallic electrode, which is probably close to reality for carbons synthesized at high temperature (which have a high electronic

conductivity). Nevertheless, even with this representation, it is possible to observe capacitance variations for porous carbons with different pore sizes and local structures. A reason for this is the packing of the ions in the pores and the resulting charge separation that occurs. The larger/more efficient the charge separation, the better the charge storage efficiency. In large pores, or at planar surfaces, *e.g.* for a positive electrode, anions will always be partly surrounded by cations as there is space for them and because there are not enough carbon atoms to compensate the ionic charge. Hence, the charge stored on the carbon will be limited by the proximity of positive charges from the cations and the fact that the anion cannot affect a large number of carbon atoms. In small pores, the anion will lose its coordination shell from the cations as well as its solvation shell. The anion will be closer to a larger number of carbon atoms that it will affect. The avoidance of positive charges from the cations and the short distance between the anion and the carbon atoms will thus lead to a better charge storage efficiency. Another way of saying this is that for a given ionic charge, the charge developed on the carbon will be higher, thus with the same amount of ions, the charge storage will be higher.

**George Zheng Chen** responded: I appreciate this insightful explanation, although my original question was related to the origin of charge storage capacity on the carbon side or even inside the solid phase of carbon. The pore structure can affect the distribution and amount of charge balancing ions, and hence the overall capacitive performance. However, it is the response, but not the origin of the charge storage capacity of the carbon, particularly that beyond the predicted values from the specific surface areas.

**Céline Merlet** said: Following up on my previous comment, I think it is important that molecular dynamics simulations are extended to the representation of defects and functionalities at the surface of the carbon electrodes as these defects/functional groups lead to large changes in the capacitances and rate capabilities of supercapacitors. Simulation techniques are not ready for this yet as the electrode is currently represented as a metallic material, which is a good assumption for porous carbons synthesised at high temperatures but is not realistic for some types of carbon structures. When defects/functionalities are present, quantum capacitance can arise on top of the double layer capacitance. This has to be taken into account to realistically model different porous materials. There is thus a need to develop a representation of the electrode which includes the quantum capacitance as well as a suitable model for the interactions between the electrolyte and the functionalities. This is definitely a direction theoreticians should explore, keeping in mind that representing these effects is not trivial.

**George Zheng Chen** asked: What is inside the solid carbon phase (not the pores) that is responsible for charge storage?

**Yury Gogotsi** replied: It is disordered, primarily  $sp^2$ -bonded (graphitic) carbon. Ref. 1 provides information about the structure and composition of carbide-derived carbons. The ordering of the carbon increases and the content of functional groups on the surface decreases with increasing annealing temperature. The effect of vacuum annealing on CDC structure is described in ref. 2.

- 1 V. Presser, M. Heon and Y. Gogotsi, Carbide-Derived Carbons - From Porous Networks to Nanotubes and Graphene, *Adv. Funct. Mater.*, 2011, **21**(5), 810–833.
- 2 S. Osswald, J. Chmiola and Y. Gogotsi, Structural Evolution of Carbide-Derived Carbons upon Vacuum Annealing, *Carbon*, 2012, **50**(13), 4880–4886.

**Céline Merlet** addressed Yury Gogotsi and George Zheng Chen: My comment is that the electrode is actually already wet at zero applied potential as is usually seen in experiments<sup>1</sup> and was also observed in molecular dynamics simulations.<sup>2</sup> For the voltages studied in the molecular dynamics simulations, it was shown that the charge storage is not linked to ions entering the pores but to an exchange of ions between the bulk and the electrodes. The total volume of electrolyte in the pores was constant when changing the potential, but the ratio of anions with respect to cations was evolving such that the liquid inside the pores was not neutral. The charge is then compensated by the charge developed on the carbon electrode. The fact that ions are already adsorbed at zero potential doesn't mean that the electrode is charged, it just means that the numbers of anions and cations in the electrode are equal when there is no applied potential. Locally, small charges can be developed on the carbon, but the overall charge on the electrode is zero. To understand a little better the different capacitances observed for different carbon structures, molecular dynamics situations looking at solvation numbers and local charges on the carbon were conducted.<sup>3</sup> The main conclusion of this study was that the more confined the ions are, the more desolvated/decoordinated they are and the more efficient is the charge storage. The structure of the porous carbons allows for a good charge separation when a potential is applied between the electrodes, thus allowing an efficient energy storage.

1 For example by NMR, see A. C. Forse *et al.*, *J. Phys. Chem. C*, 2014, **118**, 7508.

2 C. Merlet *et al.*, *Nature Materials*, 2012, **11**, 306.

3 C. Merlet *et al.*, *Nature Comm.*, 2013, **4**, 2701.

**George Zheng Chen** answered: I agree with you about how the solution side of the carbon/electrolyte interface (double layer) affects the capacitance of the material, but I am more interested in knowing how the carbon side of the interface contributes to charge storage.

**George Zheng Chen** enquired: Your analysis and explanation about the effect of the pore structure of carbide derived carbon on the capacitive performance is very interesting and insightful. This consideration is obviously focused on the electrolyte side of the double layer. I would be grateful if you could explain if the changes in the porous structures of the carbon might have also brought about variation in the charge storage capacity on the carbon side, particularly when the carbon changes from amorphous to partially graphitized and fully graphitized structures.

**Yury Gogotsi** replied: Yes. Quantum capacitance, surface area and the pore size of the carbon affect the capacitance of the carbon-electrolyte system. They all change as the CDC structure changes from amorphous to graphitic.

**Fernanda Juarez** commented: My comment is about whether the ions inside of the pores are charged or not and the nature of the interaction between them. We have studied the insertion of cations in several nanotubes in a previous publication,<sup>1</sup> concluding that the main force driving this process is the image interaction between the ions and the nanotube walls. In addition to this, we have observed more interesting features in new simulations that are not yet published. The first one is that the same electrostatic force arises between halogen anions and carbon nanotubes. The second and more important observation is that there is a correlation between the ratio of the nanotube diameter to the ionic radius and the position of the ion in the tubes. When this ratio is large enough, the ion adsorbs near to the wall, not in the centre of the nanotube. In this case we have observed a change in the adsorption mechanism, increasing the covalent interaction and decreasing the electrostatic part. Nevertheless, even in this situation the ions (cations or anions) are still charged, and with an absolute value close to one. Therefore, after these observations, it is my opinion that it is very likely to find fully charged ions inside of the pores in the systems presented.

1 Goduljan *et al.*, *Electrochem. Comm.*, 2014, **45**, 48–51.

**Yury Gogotsi** added: I agree.

**Thomas Rabbow** said: The results from Gogotsi *et al.* show that the volume of subnanometer pores per mass increases strongly for SiC-CDC and slightly for TiC-CDC after annealing at 700 °C. Despite the strong increase of subnanometer pores for SiC-CDC, the capacitance decreases. In the case of TiC-CDC a slight increase of the capacitance is observed which corresponds to a slight gain of subnanometer pores. The pore model with pore sizes adequate for the applied ions looks confirmed for certain cases (as reported in the talk) but there are contradictions for the presented results on SiC-CDC and TiC-CDC, which limit the generalization. Therefore I would like to discuss a different view on this topic which does not fully contradict the pore model, but could extend it. It has been shown that basal and edge plane oriented graphite differs by more than an order of magnitude in differential capacitance (basal plane: 3  $\mu\text{F cm}^{-2}$  vs. edge plane: 50–70  $\mu\text{F cm}^{-2}$ ) especially after annealing.<sup>1</sup>

The substrate investigated by Gogotsi *et al.* might be regarded as a mixture of amorphous and polycrystalline carbon. The crystalline phases can exhibit an edge plane or basal plane orientation at the surface of each particle. The estimation of the edge plane orientation and the number of defects could be done by oxygen adsorption–desorption (see *e.g.* active surface area concept by Laine *et al.*<sup>2</sup>). It would be interesting to investigate the active surface area after each annealing step and to correlate it with the capacitance and the volume of different pore sizes. It is an obvious assumption that inside a pore edge plane oriented crystal faces are predominant. Therefore it can be expected that a high number of (sub)-nanometer pores enhance the active surface area and thereby the capacitance. From this point of view the decrease of gravimetric capacitance (Fig. 3 of the paper) for both samples after high temperature annealing ( $T = 1400$  °C) might be explained by fewer defects and a lower active surface area. The transitional increase of capacitance for TiC-CDC after annealing at 700 °C might result from the removal of surface groups as reported, without changing the active surface

area (which needs higher temperatures). I would be very thankful for comments on this scheme or related literature.

1 See *e.g.* J.-P. Randin and E. Yeager, *J. Electrochem. Soc.*, 1971, **118**, 711.

2 N. R. Laine *et al.*, *J. Phys. Chem.*, 1963, **67**, 2030.

**Yury Gogotsi** responded: I cannot fully agree that CDC can be regarded as a mixture of amorphous and polycrystalline carbon. We have done very extensive X-ray and neutron scattering studies<sup>1</sup> showing that as-produced CDCs have short range order but lack long-range order. Thus, they are amorphous materials.<sup>2</sup> Therefore, instead of edge *vs.* basal plane terminology, I'd discuss the presence of active sites, which can be distorted bonds, 5- or 7-member rings, ad-atoms, *etc.* They are probably responsible for differences in ion adsorption (capacitance) at the same pore size, and the number of active sites changes after annealing. Unfortunately, we still poorly understand which ones are important for achieving the highest capacitance.

1 *e.g.* J. C. Palmer *et al.*, in *Characterization of Porous Solids VIII*, RSC, 2009, Special Publication No. 318, pp. 56–63.

2 J. C. Palmer *et al.*, *Carbon*, 2010, **48**, 1116–1123.

**Thomas Rabbow** said: Independent from the very different crystal sizes of TiC-CDC and SiC-CDC, I could imagine that it makes sense to characterize the surface by the more specific oxygen adsorption–desorption (active surface area). Since oxygen gets chemisorbed at graphitic edge planes and defects it might be a more adequate measure for the surface size which contributes to the capacitance. If two carbons with a similar active surface area but different pore size distributions are compared one could divide between both effects.

**Yury Gogotsi** replied: This would be helpful. We performed thermal desorption analysis on CDC in the past,<sup>1</sup> but have not done it on the samples used in this study.

1 C. Portet *et al.*, *Thermochimica Acta*, 2010, **497**(1/2), 137–142.

**François Béguin** responded: It has been proved on different kinds of fibers (herringbone, platelet and planes parallel to the fiber axis) that both basal and edge planes contribute to capacitance, with slightly higher contribution for the edge planes. The measurement of active surface area is based on di-oxygen chemisorption; it means it measures the reactivity of carbon *vs.* di-oxygen. Therefore, it cannot be directly correlated with capacitance. By contrast, the ASA could probably be correlated with the cycleability of the system.

**Boris Dyatkin** added: We completed thermogravimetric analysis in an air environment and dynamic water vapour sorption (Fig. S3 and S4 in the ESI of the paper) to assess changes in the reactive sites on the pore walls. For water vapour sorption, we observed a direct correlation between increasing hydrophobicity and higher annealing temperatures for TiC-CDC and SiC-CDC materials. This was particularly reflected by the fact that water uptake occurred at higher relative humidity values for samples annealed at higher temperatures. Given that the overall pore size distribution did not drastically change during the process (*i.e.* no

**Table 1** Analysis of oxidation onset and oxidation profile for air TGA SiC-CDC nanoparticles

Annealing Temperature	Onset of Oxidation	Key Oxidation Temperature	Full Width at Half Maxima of Oxidation Peak
Initial	424.1 °C	566.6 °C	73.6 °C
700 °C	453.4 °C	563.4 °C	78.7 °C
1200 °C	459.1 °C	574.3 °C	55.4 °C
1400 °C	445.8 °C	592.7 °C	48.5 °C
1800 °C	529.3 °C	627.9 °C	38.0 °C

significant mesoporosity was added), the most likely explanation was the shift of H<sub>2</sub>O uptake mechanism from adsorption on functional groups to capillary action. This is expected to occur for materials with fewer functional groups and is in line with the oxygen composition data derived from TGA data collected under inert atmosphere, and XPS measurements. Furthermore, analysis of oxidation onset and oxidation profile (summarized in Tables 1 and 2) showcases a general trend of oxidation onset occurring at higher temperatures, combined with more narrow combustion profiles. This suggests a reduction in surface active sites (that would initiate oxidation at lower temperatures) and more homogeneous carbon compositions, especially after annealing at 1400–1800 °C. We are therefore likely reducing the active oxygen sites on pore walls after annealing, even at 700 °C, and begin to remove defects on pore wall surfaces only above a certain temperature treatment threshold.

**Heisi Kurig** asked: In the article, the chemical composition of functional groups was determined using XPS analysis. However, it is well known that X-rays do not penetrate materials more than 10 nm. How has it been verified that the results demonstrated can be expanded to the composition of inner pores also? Are there any other methods that support these results?

**Yury Gogotsi** answered: XPS is a surface technique. However, we did sputtering and analyzed subsurface layers as well. Also, we performed EDS analysis to determine the elemental composition. While both techniques give semi-quantitative results, they clearly show the trends in the composition change after vacuum annealing at different temperatures.

**Table 2** Analysis of oxidation onset and oxidation profile for air TGA TiC-CDC microparticles

Annealing Temperature	Onset of Oxidation	Key Oxidation Temperature	Full Width at Half Maxima of Oxidation Peak
Initial	287.8 °C	440.4 °C	63.3 °C
700 °C	380.2 °C	470.8 °C	78.0 °C
1200 °C	409.9 °C	522.2 °C	48.3 °C
1400 °C	485.1 °C	587.9 °C	47.5 °C
1800 °C	528.9 °C	619.5 °C	43.8 °C

**Dirk Guldi** enquired: Has EPR spectroscopy been employed to characterise the free radical in the carbon materials, and if so has it been used to monitor saturation/interconversion into a stable material?

**Yury Gogotsi** replied: EPR has been used to study free radicals in carbons. For example, we recently used it to study surface graphitization of nanodiamond.<sup>1</sup> The increasing sensitivity of the dangling bond EPR line width to air content was used as indication of graphitization of the external layers of the nanodiamond. We have not used EPR to study bond saturation in CDC.

1 A. M. Panich *et al.*, *J. Physics: Cond. Matter*, 2013, 25, 245303.

**Keith Stevenson** remarked: What is the defining length scale for defining the charge transfer process? It is difficult to rely on bulk characterisation techniques as they don't match the same length scale. We need more model systems that can precisely probe on a sub <2 nm scale.

**Yury Gogotsi** responded: The double layer thickness is within a few nanometers and the corresponding charge transfer processes occur at the nanometer scale. I agree that model systems (*e.g.* study of electrolytes at a single- or few-layer graphene surface<sup>1</sup>) are useful for understanding the mechanisms. However, they cannot provide the same confinement effect and I cannot suggest a good technique to probe individual ions confined in nanometer pores on a sub <2 nm scale. Therefore, we still have to rely on bulk characterization techniques when studying ions in porous carbons.

1 H. Zhou *et al.*, *ACS Nano*, 2012, 6, 9818–9827.

**Patrick Unwin** said: There was an excellent poster from van Engers *et al.* on a surface force apparatus with graphene electrodes (poster P22). In principle, this would appear to be a particularly powerful means of examining surface

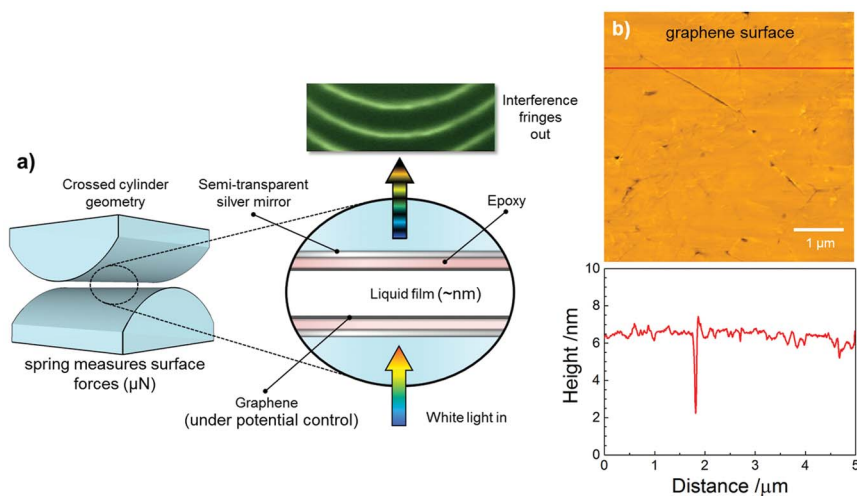


Fig. 1 The basics of the graphene surface force balance.



confinement effects, although I do not know if sufficiently close (nm and sub-nm) spacings can be achieved. I wonder if Nico Cousens, an author of the poster, could comment?

**Yury Gogotsi** added: I fully agree – this is a nice work and the technique is applicable to studying double-layer between carbon surfaces.

**Nico Cousens** answered: We have recently developed a surface force balance – also known as apparatus – with graphene surfaces (rather than conventional mica surfaces). We have successfully measured long range double layer forces in aqueous electrolytes at different graphene surface potentials. We are optimistic that we will soon be able to measure short range forces, such as those arising from layering of ionic liquids between 1–10 nm. The relevance of graphene to carbon electrodes, along with the ability to control the surface potential and confine ions to sub-nanometre gaps, will hopefully provide useful insights into surface confinement effects in (carbon based) electrochemical devices. A paper detailing the work has recently been accepted in *Langmuir*.<sup>1</sup> I have supplied a figure (Fig. 1) outlining the basics of the graphene surface force balance.

1 Britton *et al.*, *Langmuir*, 2014, **30**(38), 11485–11492.

**Boris Dyatkin** commented: The impact of quantum capacitance on total charge storage in porous carbons remains an important question. Biener *et al.*<sup>1</sup> showed how structural defects and surface groups affect the densities of state of planar graphene, and how that, in turn, affects both overall charge storage and screening of similarly charged ions. However, Kubuzono *et al.*<sup>2</sup> showed that quantum capacitance contributions remain significant only as long as the number of graphene layers remains below 4. We do not yet know whether planar graphene models can be applied to confined ions in cylindrical or slit pore configurations. Furthermore, while conventional assumption suggests that the number of graphene layers between two pores is 2 (the two pore walls), this is likely to change for different particle sizes with branched pore architectures. Furthermore, recent WAXS studies by Smarsly *et al.*<sup>3</sup> show some changes in graphene sheet stacking along the [002] direction for CDCs produced at higher temperatures. We expect that vacuum annealing likely also produces changes in the stacking, which further underscores the increased need for more extensive mathematical modeling of the structure and surfaces of porous carbon materials.

1 Biener *et al.*, *J. Phys. Chem. C.*, 2014, **118**(1), 4–15.

2 Kubuzono *et al.*, *Sci. Rep.*, 2014, **3**, 1595.

3 Smarsly *et al.*, *J. Phys. Chem. C.*, 2014, **118**(29), 15705–15715.

**Fulian Qiu** asked: In the paper, 20 nm to 2.0  $\mu\text{m}$  sized carbide-derived carbons with an average pore size of  $\sim 0.8$  nm were employed as electrode materials. Areas measured using gas adsorption should be different from effective surface areas accessible by ions in the supercapacitors. When the particle size decreases, the internal pore surface to total surface area (internal pore surface plus inter-particle pore surface) ratio will decrease. For example, if one 2  $\mu\text{m}$  particle is smashed into 20 nm particles, the total surface area of the 20 nm particles would be roughly 100 times bigger than that of the 2  $\mu\text{m}$  particle. In this way, for a supercapacitor

electrode, the inter-particle pore surface area will be much bigger for the case of 20 nm particles than for that of 2  $\mu\text{m}$  particles, and it could be comparable to the internal pore surface area for the 20 nm carbon particle electrode. If the self discharge process is controlled by internal pores, how does the particle size influence the self discharge process?

**Yury Gogotsi** answered: The inter-particle pore surface area is bigger in the case of 20 nm particles than in that of 2 micron particles, but it is a small fraction of the internal pore surface area for the 20 nm carbon particle electrode ( $>1000 \text{ m}^2 \text{ g}^{-1}$ ).

**François Béguin** opened the discussion of the paper by Asa Noofeli:† What is the meaning of ESR at 1 kHz? Similarly what is the difference between series resistance RS and ESR? Generally the ESR is defined as the intercept of a Nyquist plot with the X-axis at high frequency.

**Asa Noofeli** communicated in reply: ESR (equivalent series resistance) is the real component of the impedance measured at 1 kHz and is provided as a frame of reference as some instruments can only determine the impedance at this frequency. In this paper, RS represents the intercept of the Nyquist plot with the real axis.

**George Zheng Chen** commented: Regarding the use of 1 kHz for the resistance measurement of a supercapacitor, I think it is often sufficient for fast analysis, particularly if the interest is to monitor the trend of resistance change with a dynamic variation of voltage or pressure of the supercapacitor.

**François Béguin** asked: Ionic liquids display low electrical conductivity and high viscosity. For this reason, the authors have used carbons with a high amount of mesopores. Unfortunately, the porosity of such carbons is poorly developed and the density is extremely low. This leads to a very poor volumetric capacitance, while industry is just looking for the highest values of this parameter. The conductivity of ILs can be enhanced by increasing temperature. Unfortunately, this will lead to a decrease of stability window and consequently to losing the advantage expected of using ILs. I agree with one comment of the authors that, for stationary applications, the volume of the systems is not an important issue. If it is the case, why not to use aqueous electrolytes which are very cheap, safe and environment friendly and can be implemented with microporous carbons of high density?

**Asa Noofeli** communicated in response: Our aim of using carbons with various pore sizes was to study its effect on device performance. I agree that the chosen ionic liquids may not compare favourably with other electrolytes in terms of conductivity, nevertheless they have other advantages such as low volatility/flammability which may be useful. The relatively high viscosity could possibly be tackled by using higher operating temperatures. This is currently under investigation and unfortunately I don't have any results to present at the moment.

---

† Asa Noofeli's paper was presented by Peter Hall, University of Sheffield, Sheffield, UK.

However the operating window of aqueous electrolytes are limited and may not be suitable for all applications.

**Alexander Forse** enquired: Is it possible to modify your synthesis method to introduce some microporosity into the carbon? This may boost the energy density.

**Asa Noofeli** communicated in answer: Yes it is possible. We can modify the carbonization and activation processes to produce the required porosity. However, in the case of ionic liquid electrolytes, the presence of micropores tends to increase the overall resistance of the device.

**Julie Macpherson** asked: Water incorporation into ionic liquids is a potential problem for you, resulting in a reduction in the magnitude of the solvent window. How do you ensure against this?

**Asa Noofeli** communicated in reply: All ionic liquids are stored/handled inside an argon filled glovebox.

**George Zheng Chen** opened the discussion of the paper by Elzbieta Frackowiak: Your work on redox active electrolytes in supercapacitors is very interesting and stimulating as a new approach toward electrochemical energy storage. I would like to know how you have calculated the capacitance values for your two-electrode cell. My understanding is that for peak-shaped CVs and non-linear GCDs, the charge/voltage ratio is not the same as capacitance.

**Elzbieta Frackowiak** responded: Thank you for your encouraging comment. Capacitance values were verified in two different ways. Full time of discharging was considered for the first method, giving the higher value of capacitance, however, the energy extracted from this low voltage region is doubtful. For more reliable calculations, we considered only the slope of the linear part of the galvanostatic profile (0.2–1.0 V); such a method gave slightly lower values but we find them more appropriate. It is noteworthy that capacitors based on iodide aqueous solutions demonstrate excellent cyclability, especially with stainless steel current collectors.

**George Zheng Chen** asked: In Fig. 4 and 8 of the paper, it can be seen that the gain of charge storage is at low cell voltages, which means the storage is low in energy content.

**Elzbieta Frackowiak** answered: I agree that, in the low cell voltage region, energy storage is very moderate in the case of the hydroquinone additive (Fig. 4 and 5 of the paper) as well as in iodide solutions (Fig. 18 of the paper), however, integrating the total charge with a smart electrochemical configuration might even efficiently exploit this low cell voltage region.

**George Zheng Chen** remarked: The diffusion or transport of the redox active species inside the activated carbon layer should have a strong influence on the

charge storage behaviour. How thick and how porous was the activated carbon layer on the electrode, because the redox active species are not anchored on the electrode surface, and can diffuse back to the bulk electrolyte after charging or discharging, and then become irrecoverable? This may contribute to self-discharge. However, because the redox reactions occur at low voltages, such diffusion induced self-discharge may not be observed before the cell voltage decay from self-discharge of the charge stored in the double layer has come to a sufficiently low value.

**Elzbieta Frackowiak** replied: The thickness of the electrode was 300  $\mu\text{m}$ . The specific surface area of the carbon electrode was 20% lower than the pristine activated carbon powder. The total pore volume of the electrode was 1.039  $\text{cm}^3 \text{g}^{-1}$ , the micropore volume was 0.716  $\text{cm}^3 \text{g}^{-1}$ , whereas the mesopore volume was equal to 0.269  $\text{cm}^3 \text{g}^{-1}$ . The redox active species, depending on their type, can be partly grafted or immobilized into the carbon network (*e.g.* hydroquinone species) or specifically sorb/interact with the carbon structure in the case of iodide species, giving C-I binding. In the literature it has been found that iodine can play the role of a p-dopant of carbon and even increase its conductivity. Concerning the carbon texture, it has been shown by us that mesopores play a crucial role for the redox activity of the iodide/iodine couple, because they match very well with the size of polyiodides (the final product of redox reactions). The concentration of iodide ions in the electrolyte bulk is quite high in comparison to the charge utilised during the charging/discharging process, so even if some part of the process would be irreversible, we believe that the concentration of ions preserves the high efficiency of the charge/discharge process.

Regarding self-discharge – we measured this value over 24 h after full charging to 0.8 V and we observed 200 mV of self-discharge, with a significant drop of voltage during the first two hours.

**Fulian Qiu** remarked: In Fig. 17 of the paper, does the capacitance as a function of floating time show different trends from two different calculation procedures? In the two-electrode supercapacitor configuration, on the anode, iodide ions were oxidized to form iodine, and the iodine diffused away from the electrode surface, then combined with iodide to form complex species; this would depend on the time scale in the CV and charge-discharge process (scan rates and charge/discharge currents). On the cathode, it should be pure double-layer charge-discharge responses initially or on a shorter time scale. The device is an asymmetric supercapacitor. During the long duration floating experiments, complex species generated in the anode region could diffuse through the separator to the cathode surface, and electrochemical reduction processes occur on the electrode surface depending on the separator structure. In this way, the supercapacitor would be a battery. As asymmetric supercapacitors are different from pure electrochemical double-layer supercapacitors, charge-discharge processes are much slower in asymmetric supercapacitors, their discharge curves are not linear, and it is difficult to calculate capacitance using the slope accurately. The total discharge time method for the capacitance calculation would be more proper.

**Elzbieta Frackowiak** answered: We do agree that the redox activity of iodide species might suggest a battery type behaviour, but it is solely connected with the positive electrode. When separating the voltammetry responses for both electrodes, the positive electrode shows a very well defined peak in a narrow range of potential (according to iodine activity from the Pourbaix diagram). This high additional capacitance originates from iodide-based redox couples, formed during polarisation of the positive electrode. However, the total capacitor presents quite a rectangular shape of the cyclic voltammogram as well as a triangular shape of the galvanostatic profile, that allows us to consider such a system as a capacitive one with a significant contribution from pseudocapacitance. Typically, the slower the regime, the more significant the contribution from Faradaic reactions. Of course, we can assume that during long term cycling, the redox species diffuse between the electrodes creating a battery type response; but we would like to note that, even after several thousand of cycles, the major part of the galvanostatic profile is triangular (Fig. 18 of the paper), without any remarkable plateau induced by a 'pure' redox response. Hence, we decided to calculate the capacitance value using two possible methods typical for evaluation of capacitor performance (Fig. 17 of the paper). Remarkably, we noticed that after long-term cycling, the pH of the electrolytic solution changed from a neutral one to more alkaline (close to 8). Hence, the gradual aggravation of capacitor performance after durable cycling could be explained by pH change. We proved that iodates formed in a more alkaline medium show definitively worse performance (low capacitance values, poor solubility).

**George Zheng Chen** asked: Diffusion of the redox active species in the electrolyte should have played a role in the rate of charging and discharging. Fig. 4 of the paper shows the CVs recorded at  $5 \text{ mV s}^{-1}$ , what may happen if the scan rate is increased, say to  $100 \text{ mV s}^{-1}$ ? On the other hand, the redox reaction only occurs in a particular and narrow range of electrode potentials or cell voltages. What cell voltage was applied for recording the impedance data presented in Fig. 6, 7, 8, 9, 16 and 20 of the paper?

**Elzbieta Frackowiak** responded: The redox response gradually disappears with an increase of scan rate; Faradaic reactions are typically limited by diffusion. At a scan rate of  $100 \text{ mV s}^{-1}$  we observed a more resistive behaviour of the CV profile, especially in the case of a hydroquinone additive in acidic solution (Fig. 4 of the paper). The impedance spectra in Fig. 6, 7, 8, 9, 16 and 20 of the paper were recorded at open circuit voltage (OCV).

**Chi-Chang Hu** queried: From a comparison of the CV curves shown in Fig. 1 in the text, how can the double-layer capacitive currents in the whole investigation potential region be significantly enlarged by adding dissolved electroactive species (e.g.  $\text{H}_2\text{Q}$  here)?

**Elzbieta Frackowiak** answered: The cyclic voltammogram presented in Fig. 1 of the paper concerning the activity of hydroquinone in an acidic medium has been recorded after 500 subsequent voltammetry cycles (similar to the profile shown in Fig. 4 of the paper). Capacitive current response combines electrostatic attraction of ions together with Faradaic reactions (Fig. 10 of the paper). Separation of the

EDL response and the Faradaic one might be possible by applying different scan rates (CV), current regimes (galvanostatic loading) or studying time constant values by electrochemical impedance spectroscopy. It has to be noted that the Faradaic response of porous electrodes does not reflect the typical peak profile observed for non-porous electrodes.

**Dirk Guldi** asked: Has the pH dependence of the different diols been investigated, especially with respect to the reversibility of the redox chemistry, that is, oxidation and reduction of the diole ?

**Elzbieta Frackowiak** responded: Various diols with different OH group substitutions have been investigated in neutral, alkaline and acidic media to prove a significant role of protons in their redox chemistry. Fig. 1 of the paper clearly shows the highest redox activity of 1,4-dihydroxybenzene (hydroquinone) in acidic and alkaline electrolytic solutions. Unfortunately, the reversibility of the redox activity is moderate, especially in an acidic medium (1 mol L<sup>-1</sup> sulfuric acid).

**Fulian Qiu** opened the discussion of the paper by François Béguin by commenting: In Fig. 20 of the paper, does the charge-transfer resistance increase with floating time? In fact, there are two charge-transfer processes; two processes become more distinguishable with floating time. If the processes are from the anode electrode only, they originate from the current collector-carbon layer interface and electrochemical reaction on the carbon surface.

**Yury Gogotsi** asked: What electrochemical reaction occurs when sodium molybdate salt is added? Is there any deposition of molybdenum oxide or other reaction products on carbon?

**François Béguin** answered: Addition of sodium molybdate (Na<sub>2</sub>MoO<sub>4</sub>) to 1 mol L<sup>-1</sup> Li<sub>2</sub>SO<sub>4</sub> causes an increase in the conductivity of the electrolyte mixture resulting in enhanced EDL capacitance up to 0.8–1.0 V. When the voltage is increased up to 1.6 V, pseudofaradaic contributions due to the presence of MoO<sub>4</sub><sup>2-</sup> (equilibria (3) and (4) in the manuscript) and reversible hydrogen storage come into play at the negative electrode. In post-mortem investigations of capacitors after floating at 1.6 V for 120 h, we could detect a MoO<sub>2</sub> deposit on the negative stainless steel current collector at the periphery of the AC electrode. Besides, no deposit was observable on the positive side due to the negative shift of potential as explained in the manuscript. Further investigations are in progress to analyze the carbon electrodes and especially to detect MoO<sub>2</sub> in the negative one.

**Chi-Chang Hu** remarked: The speaker demonstrated that the AC/AC system can achieve 2.2 V in aqueous media containing Li<sub>2</sub>SO<sub>4</sub>. However, after the floating test, it is not stable even at 1.6 V if the electrolyte does not contain Na<sub>2</sub>MoO<sub>4</sub>. What happens to the positive and/or negative electrodes? Why does Na<sub>2</sub>MoO<sub>4</sub> improve the cycle stability of carbon? Was Na<sub>2</sub>MoO<sub>4</sub> deposited onto the carbon electrodes?

**François Béguin** replied: In ref. 10–11 of the manuscript, it was demonstrated from galvanostatic charge–discharge cycling – where the cell voltage only stays

temporarily at the specified value – that the AC/AC systems are able to operate up to ~2 V, while using gold current collectors. When using stainless steel current collectors and potentiostatic floating – which is to keep the cell at such a high voltage for a long period of time (120 h) – the maximum voltage in 1 mol L<sup>-1</sup> Li<sub>2</sub>SO<sub>4</sub> is 1.5 V. At voltages higher than 1.6 V, carbon is oxidized at the positive electrode and the current collector is corroded, which leads, after some floating time, to a drop of capacitance and an increase of resistance (detailed information is given in ref. 12–13 of the manuscript). When Na<sub>2</sub>MoO<sub>4</sub> is added to the electrolyte, the maximum potential of the positive electrode is shifted to lower values, and consequently at a voltage of 1.6 V the positive electrode is not oxidized. A MoO<sub>2</sub> deposit was detected on the negative electrode, according to equation (3) of the manuscript.

**Chi-Chang Hu** continued: Due to the enlargement of capacitance as well as the increase in the iR drop of the resultant cell with floating test time, there should be a certain relationship between the formation of oxygen-containing functional groups and the floating test time. What is the role of Na<sub>2</sub>MoO<sub>4</sub> during the floating test period with regard to protecting the oxidation/functionality of activated carbon on both electrodes?

**François Béguin** answered: In our previous works (ref. 12 and 13 of the paper), we demonstrated that under floating conditions at or beyond 1.6 V, oxygenated functionalities are developed on the positive electrode, resulting in an increase of resistance and decrease of capacitance. This happens mainly because the maximum potential of the positive AC electrode is above the water oxidation potential limit, and obviously the amount of oxygenated surface functionalities increases with the floating time. However, the resistance increase is also partly due to the generation of corrosion products on the positive stainless steel current collector which accumulate at the AC/collector interface. When MoO<sub>4</sub><sup>2-</sup> is added to the electrolyte, the maximum potential of the positive AC electrode is lowered by about -0.162 V for an operating voltage of 1.6 V, *i.e.* below the oxidation limit of water, preventing the oxidation of carbon and corrosion of stainless steel.

**Laurence Hardwick** opened the discussion of the paper by Yong Cao: What is the mechanism of catalysis in your system, *i.e.* how does the catalyst work?

**Yong Cao** replied: Thank you for your question. The mechanism of Li-O<sub>2</sub> batteries is now unclear due to the use of different catalysts and electrolytes. In our previous work, we just searched for some effective catalysts and constructed the Li-O<sub>2</sub> battery test system. Now, we are proceeding with some deep study of the mechanism through *in situ* XRD and Raman and also XPS.

**Laurence Hardwick** continued: As you form a solid discharge product on the cathode surface, it is hard to imagine in a conventional sense how the catalyst works?

**Yong Cao** answered: This is a good comment. Some soluble catalysts have been reported with improved performance, which may be a research hot topic in the future.<sup>1,2</sup>

- 1 H.-D. Lim *et al.*, *Angew. Chem.*, 2014, **126**, 4007–4012.  
2 Y. Chen *et al.*, *Nat. Chem.*, 2013, **5**, 489.

**George Zheng Chen** asked: In your work, what is defined as a catalyst? Can you give experimental demonstration of the catalysis as you have claimed?

**Yong Cao** responded: Thanks for your question. In Li-O<sub>2</sub> batteries, the discharge and charge reactions contain oxygen reduction and evolution reactions, but the sluggish kinetics of the oxygen electrode result in large discharge and charge overpotentials. So a catalyst is important to improve the kinetics of the oxygen electrode. In our work, when using the CoFe<sub>2</sub>O<sub>4</sub>-rGO composite as the cathode, the discharge overpotential, especially the charge overpotential, is significantly reduced compared with pristine rGO. Also, the capacity was improved.

**George Zheng Chen** continued: Would you please explain what results in your work show the catalytic activity as you have stated in the title of your paper? In other words, what electrode reactions have been catalysed and how?

**Yong Cao** replied: Both the discharge and charge overpotentials were significantly reduced, which can be attributed to the catalytic activity of the CoFe<sub>2</sub>O<sub>4</sub>-rGO composite, compared with the pristine rGO.

**Chi-Chang Hu** said: For Li-air batteries, the preferred product of the cathode is Li<sub>2</sub>O<sub>2</sub>. What is the preferred electron transfer number of the catalyst? From the preferred product, the preferred electron transfer number is 2. Can the authors obtain the preferred products and better performances if using a catalyst with the electron transfer number of the ORR equal to 2?

**Yong Cao** responded: Indeed, a catalyst with a 2-electron process would benefit the formation of the ideal product Li<sub>2</sub>O<sub>2</sub>. But in fact, the ORR process in the non-aqueous system is not similar to that in the aqueous system. The key issue in current Li-O<sub>2</sub> batteries is not the discharge process, but the charge process. Li<sub>2</sub>O<sub>2</sub> has been confirmed as the discharge product in different electrolytes with different catalysts. However, some side-products form in the charging process due to either the oxidation of carbon in the presence of Li<sub>2</sub>O<sub>2</sub> or the decomposition of electrolytes on the carbon surface. These side products, such as Li<sub>2</sub>CO<sub>3</sub>, are not easily electrodecomposed during charging, and thus result in a large overpotential and low round-trip efficiency.

**Wanjing Yu** said: I am just wondering if it is possible to calculate the specific capacity of CoFe<sub>2</sub>O<sub>4</sub>? The mass of rGO is only 17.3%. The CoFe<sub>2</sub>O<sub>4</sub> might also contribute to the capacity. Is it reasonable to calculate the specific capacity based only on the mass of rGO?

**Yong Cao** replied: In early works, the capacity was calculated based on the mass of carbon in the electrode. We also provide the specific capacity based on the total mass of rGO + CoFe<sub>2</sub>O<sub>4</sub> on the top axis of Fig. 3 of the paper. In fact, CoFe<sub>2</sub>O<sub>4</sub> contributes no capacity in the voltage window of 2.2–4.2V.



**Laurence Hardwick** remarked: Did you use any other characterisation tools to confirm the composition of the discharge product ( $\text{Li}_2\text{O}_2$ )?

**Yong Cao** responded: Yes, we have also conducted XRD and Raman, but the signals were not so strong, which may be ascribed to the poor crystallinity of the  $\text{Li}_2\text{O}_2$ . But we are trying to improve it.

**Laurence Hardwick** continued: Does  $\text{Li}_2\text{O}_2$  have a clear and distinct signal in XPS?

**Yong Cao** added: Yes, the binding energies of Li-O in  $\text{Li}_2\text{O}_2$  and  $\text{Li}_2\text{CO}_3$  are different from each other. You can refer to ref. 1.

1 S. Liu *et al.*, *Adv. Energ. Mater.*, 2014, 4, 1301960.

**Robert Dryfe** asked: In the experimental section you state that an atmosphere of oxygen is used to perform the experiments. However, can you be sure that there is no residual carbon dioxide in your sample? In other words, is it possible that the carbon deposits come from reduction of atmospheric  $\text{CO}_2$ , rather than reaction of the lithium salts with the reduced graphene oxide?

**Yong Cao** answered: We used a modified vacuum drier as the test device in which our batteries were placed. The vacuum drier was firstly evacuated and then filled with high purity oxygen. So we can exclude the influence of  $\text{CO}_2$  from the atmosphere.

**Surbhi Sharma** enquired: Did you perform any XPS studies on your  $\text{CoFeO}_4$ -rGO samples to check for any residual impurities and the C:O ratio in GO and rGO?

**Yong Cao** replied: I am sorry to tell you that I did not do the work you mentioned.

**Dirk Guldi** opened the discussion of the paper by Laurence Hardwick: What is the rationale for the Raman shift ?

**Laurence Hardwick** answered: The rationale for the Raman shift of the 2D band is that it occurs from charge transfer onto the graphene sheets of the graphite intercalation compound, and from where the graphene layers are flexible and deform around domains of intercalating lithium ions in stage 3 and 4 GICs in particular. We will be investigating separating out the relative contributions in the near future.

**Dirk Guldi** continued: What is the local and overall concentration of lithium between the graphene sheets upon intercalation?

**Laurence Hardwick** responded: The stage 3 GIC, where we see the shift of the 2D band, has the formula  $\text{LiC}_{18}$ .

**Christopher Sole** commented: The large downshifting of the 2D Raman peak for our graphite electrodes upon stage 4 and stage 3 formation (0.2–0.15 V vs. Li) may be related to strain (or at least doping induced bond expansion) as suggested by Chacón-Torres *et al.*<sup>1</sup> in K<sup>+</sup> intercalated graphite intercalation compounds. This paper claims that the disappearance of the 2D peak for stage 2 and stage 1 compounds is due to excessive charge on Li bounding layers, thus the observed 2D peak for stage 4 and stage 3 comes from the nonbounding (interior) graphene layers which are much less charged. The split G peak at high stage number also suggests strain as the downshift of the interior G peak can be explained by bond expansion and not doping. Interestingly, this strain argument was briefly proposed by W. W. Huang and R. Frech in 1998<sup>2</sup> without looking at the 2D band.

1 Chacón-Torres *et al.*, Manifestation of Charged and Strained Graphene Layers in the Raman Response of Graphite Intercalation Compounds, *ACS Nano*, 2013, 7, 9249.

2 W. W. Huang and R. Frech, *In Situ* Raman Studies of Graphite Surface Structures during Lithium Electrochemical Intercalation, *J. Electrochem. Soc.*, 1998, 145, 765.

**François Béguin** said: You conclude that your Raman data support the Dumas–Herold model of lithium intercalation. However, there is not a clear statement of the experimental information which allows you to draw such a conclusion. Could you explain which experimental data allow you to discriminate between the Rüdorff and Dumas–Herold models?

**Laurence Hardwick** replied: We hypothesise that the significant shift of the 2D band is the result of charge transfer and the deformation of graphene layers around domains of intercalating lithium ions. In the Rudorff model the ions enter into discrete layers – causing no deformation. In the Dumas–Herold model the graphene layers are required to slightly deform. In addition, as has been experimentally observed by us and before by M. Inaba, H. Yoshida and Z. Ogumi (ref. 13 in the paper), the G-band is seen to shift which can be explained by the presence of a dilute stage 1 graphite intercalation compound – again supporting the Dumas–Herold model in which intercalants are present within each layer.

**Yury Gogotsi** asked: How can you separate contributions from charge transfer and mechanical strain?

**Laurence Hardwick** answered: We are looking into experiments to do this – as suggested from this discussion. Certainly computational modelling, pdf and strain studies will be important to understand these contributions. A comment that we stated in the paper is that the graphene sheets deform around the lithium intercalated domains. We admit we have to be careful in calling this ‘strain’ as this is a larger scale property of the whole material.

**Yury Gogotsi** addressed Christopher Sole and Laurence Hardwick: Did you compare the Raman shift after intercalation to the Raman shift of graphite (graphene or carbon nanotubes) subjected to purely mechanical stress?

**Laurence Hardwick** responded: No, we have not done so. In the literature there are many investigations looking at mechanical stress on various forms of carbon – but I am yet unaware of any studies looking at the effect of mechanical stress on

the Raman spectrum of graphite intercalation compounds (GICs). Certainly this type of study will be important in understanding the role of localised graphene sheet deformation in stage 2, 3, 4 GICs.

**Christopher Sole** added: We have not attempted such a measurement although it could be a good idea, the literature values for graphene depend a lot on substrate, preparation and laser used so it is difficult (not impossible!) to compare. The effect of uniaxial stress splits the 2D band so we can rule this out. Biaxial stress (as we propose) should have a similar downshifting effect, however, we need to take care to separate the effects of doping and strain. This may be possible using a technique similar to Lee *et al.*,<sup>1</sup> but they say this is limited to SLG and possibly difficult due to the dispersion of the 2D peak with laser wavelength (we use 633 nm in the paper).

1 Lee *et al.*, Optical separation of mechanical strain from charge doping in graphene, *Nat. Commun.*, 2012, 3, 1024.

**Yury Gogotsi** continued: You may wish to conduct X-ray pair distribution function (PDF) analysis of intercalated samples to determine if there is a change in carbon-carbon bond length, and compare the observed strain to that measured by Raman spectroscopy.

**Laurence Hardwick** replied: That is an excellent suggestion, which we had not previously considered and would be a complementary measurement technique to probe structural changes at various stages in graphite intercalation compounds.

**Keith Stevenson** remarked: Does the 2D peak broaden as a function of lithiation potential? It is not clear how the intensity decreases and peak width changes (table 2 of the paper). They should be correlated.

**Laurence Hardwick** responded: As the intensity of the 2D(1) peak decreases so does the FWHM generally, although possibly the peak width may be obscured by background at low peak intensity. The 2D(2) peak is relatively sharp and intense at the beginning and end. It broadens and increases in intensity as it shifts dramatically (at 0.2 V stage formation) although possibly this is due to incorporating leftover 2D(1) intensity. In short, it is challenging with current data (signal to noise ratio) to separate the contributions from the 2D(1) and 2D(2) peaks.

**Keith Stevenson** continued: It is not clear how the 2D overtone is reflective of compressive strain and buckling of the sheet, as the resolution of this band is low.

**Laurence Hardwick** answered: After our conversation I agree with your point we should avoid using the term strain. We hypothesise that what we observed is a localised distortion of the graphene sheet due to the distribution of lithium domains within the graphitic structure, and this is reflected by the shift in the 2D peak.

**Keith Stevenson** added: Do different particles show the same trends with lithiation/delithiation?

**Laurence Hardwick** replied: This is a good point. Certainly, in past Raman studies<sup>1</sup> we observed variation in lithium concentration at low current densities during lithiation. We have not looked at multiple points in this instance yet for the 2D peak. This heterogeneity of lithium insertion into practical graphitic electrodes is an interesting observation that has been observed by many authors – such as Aurbach, Kostecki, Novak and Yazami.<sup>2–5</sup> However single point measurements on other graphitic carbons (as yet unreported by us) show similar trends for the 2D band to those reported within the Faraday paper.

1 L. J. Hardwick *et al.*, *Solid State Ion.*, 2006, **177**, 2801–2806.

2 E. Markevich, G. Salitra, M. D. Levi and D. Aurbach, Capacity fading of lithiated graphite electrodes studied by a combination of electroanalytical methods, Raman spectroscopy and SEM, *J. Power Sources*, 2005, **146**(1–2), 146–150.

3 R. Kostecki and F. McLarnon, Microprobe study of the effect of Li intercalation on the structure of graphite, *J. Power Sources*, 2003, **119–121**, 550–554

4 P. Maire, A. Evans, H. Kaiser, W. Scheifele and P. Novak, Colorimetric determination of lithium content in electrodes of lithium-ion batteries, 2008, *J. Electrochem. Soc.*, **155**(11), A862–A865.

5 Y. Reynier, R. Yazami and B. Fultz, XRD evidence of macroscopic composition inhomogeneities in the graphite–lithium electrode, *J. Power Sources*, 2007, **165**(2), 616–619.

**Alexander Forse** said: Have you performed any quantum chemistry calculations of the Raman frequencies for different intercalation stages? This could offer some insight into the mechanism and help distinguish between the different intercalation models mentioned in the paper.

**Laurence Hardwick** answered: This is an excellent suggestion – and no, we have not performed any calculations. We recognise that we will require these types of calculations to investigate whether the effect we see (*i.e.* the large downshift of the 2D band) can be wholly attributed to doping, or may also include a contribution from highly localised deformation of graphene layers around intercalated lithium domains.

**Dirk Guldi** asked: Are you considering Raman mapping to probe local disorder, stress, *etc.*?

**Laurence Hardwick** replied: Yes – we are considering mapping to probe multiple areas of the electrode to see if band shifts are uniform across the electrode surface.

**Dirk Guldi** continued: Have you changed the excitation in your Raman experiments to see if the effect on the 2D band shift and shape is wavelength dependent?

**Laurence Hardwick** responded: We have not done these measurements yet – and we plan to do so. We would expect to see a shift as the first order D-band has been shown to be excitation energy dependent. Looking at the data from Chacón-Torres *et al.*<sup>1</sup> on CxK compounds, they use a different wavelength laser and see a different wavenumber shift.

1 Chacón-Torres *et al.*, Manifestation of Charged and Strained Graphene Layers in the Raman Response of Graphite Intercalation Compounds, *ACS Nano*, 2013, **7**, 9249.

**Dirk Guldi** asked: How do you intercalate lithium into graphite?

**Laurence Hardwick** replied: We are intercalating the lithium ions electrochemically, using a sealed *in situ* cell.

**Katherine Holt** addressed François Béguin and Laurence Hardwick: This is a question about the proposed models for Li ion intercalation into graphite. In the Rudorff model shown in Fig. 7 in the paper, Li is seen inserting between only some of the layers and not others. If this model is correct, what determines which layers (and how many) the Li will insert into? Is this statistical or is there a chemical preference for particular layers?

**François Béguin** answered: You asked exactly a good question about the Rudorff model: “why the reagent would select particular intervals and not others?”. This model is perfect to account for the X-ray diffraction data but not to explain the reactivity of graphite with stage changes. This is the reason why the Daumas–Herold model has been introduced, in order to express that all intervals are equivalent; simply the reagent occupies a part of these intervals, being separated by pleats from the unoccupied regions.

**Laurence Hardwick** added: The Rudorff model was the earliest structural model to explain PXRD data of graphite intercalation compounds (GICs). All undergo an increase of the separation between the graphene sheets, the *d*-spacing (3.35 Angstroms). For lithium GICs this separation increases by 10% to 3.7 Angstroms. It could be argued that there is an additional energy barrier for the insertion of the first Li<sup>+</sup> for the separation increase – for it to squeeze in – which is then removed for the second Li<sup>+</sup> as the gap has already widened (unless of course the 1<sup>st</sup> Li<sup>+</sup> has diffused sufficiently into the bulk and the interface has relaxed back to the original separation). What I believe is that there is no chemical preference for a particular layer insertion (there is the added complication of solid electrolyte interphase formation – adding to the distribution of interfacial resistances in a porous electrode). I believe that in the initial stages of electrochemically driven intercalation there is a dilute stage; one GIC in which all layers have a diffuse amount of Li<sup>+</sup> inserted.

**François Béguin** continued: Does the 2D band show evidence of the dilute 1<sup>st</sup> stage?

**Laurence Hardwick** responded: The 2D band does shift moderately during the dilute stage 1 by *ca.* 22 cm<sup>-1</sup> V<sup>-1</sup>. The G-band shifts by *ca.* -28 cm<sup>-1</sup> V<sup>-1</sup> during the dilute stage 1 phase (*ca.* 0.55 to 0.22 V *vs.* Li/Li<sup>+</sup> (See Fig. 6 in the paper). This effect is likely to be from doping of the graphene layers.

**Boris Dyatkin** stated: It would be interesting to implement this *in situ* Raman spectroelectrochemistry approach to analyze anion intercalation into graphite cathodes. Read *et al.*<sup>1</sup> presented evidence that anion insertion likely produces stage 1 intercalated graphite at 5.2 V. Observing changes in the 2D band of the material during PF<sub>6</sub><sup>-</sup> or BF<sub>4</sub><sup>-</sup> intercalation would yield novel insights into changes in the graphite structure.

1 Read *et al.*, *Energy Environ. Sci.*, 2014, 7(2), 617–620.

**Laurence Hardwick** replied: Yes I would agree with this comment. We have in the past looked at the G and D bands during  $\text{BF}_4^-$  intercalation,<sup>1</sup> but we have not looked at the 2D band yet, but plan to do so.

1 L. J. Hardwick *et al.*, An *in situ* Raman study of the intercalation of supercapacitor-type electrolyte into microcrystalline graphite, 2006, *Electrochim. Acta*, 52(2), 675–680.

**Richard McCreery** said: When you see the shift in the 2D band position during lithium ion intercalation, do you see a corresponding shift in the D band?

**Laurence Hardwick** answered: Unfortunately the D-band (when clearly visible – if we are measuring in a more ‘disordered’ area) weakens and then vanishes into the signal noise on initial  $\text{Li}^+$  insertion, before any shift in the 2D band is observed, *ca.* by 0.8 V *vs.*  $\text{Li}/\text{Li}^+$ . The weakening of the D-band is shown in ref. 12 of the paper. We would be motivated to try to measure  $\text{Li}^+$  intercalation into a more highly disordered carbon – to see if we could measure any D-band shift before the signal fully disappears.