

acid electro-oxidation is, however, not fully understood because there are several competing reaction steps and several possible reaction intermediates.

The reaction is thought to occur through two possible pathways: a direct pathway that forms CO_2 via an unknown intermediate, and an indirect pathway in which formic acid is broken down to H_2O and CO , which is subsequently oxidized to CO_2 . Now, Timo Jacob from the Universität Ulm and colleagues have used density functional theory to better understand the roles played by CO and OH in the direct oxidation of formic acid. Previous studies have suggested that the direct route to CO_2 proceeds through two possible intermediates, HCOO or a transient COO intermediate. Jacob and colleagues have now calculated the effect that CO and OH have on the energy barriers of these two processes and thus on the overall oxidation of formic acid.

Carbon monoxide is known to poison the surface of the platinum electrode by blocking active sites, but the researchers also found that CO increases the associated reaction barriers, suppressing formic acid oxidation further. The effect of OH was only minor. Surprisingly, however, they saw that when low concentrations of both CO and OH were present the reaction could actually be promoted, reversing the overall poisoning effect of CO . Jacob and colleagues suggest that this was because of changes to the aqueous hydrogen-bonding network at the electrode surface — which is weakened when both CO and OH are present — and the surfaces charges that they induce. GA

CRYSTALLINE MATERIALS

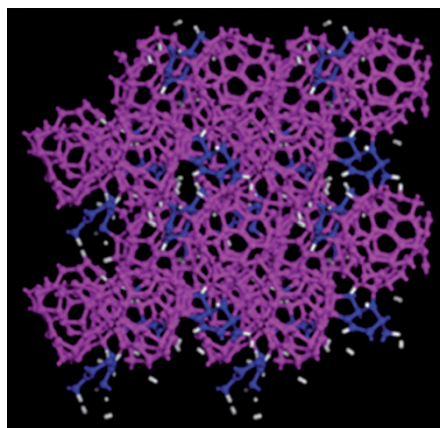
Disorder is in order

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The characteristics of solid-state materials are inherently linked to the order — or lack thereof — in which their atoms are arranged. Leaving aside the notorious exception of exotic quasicrystals, which show short-range order yet lack long-range periodicity, most material domains are either amorphous or crystalline, and can deviate from these ideal states through the presence of short-range order or defects, respectively. In contrast, by preparing a crystalline material whose building blocks are amorphous carbon clusters, a team from Jilin University and several institutions in the United States, led by Lin Wang, have now hybridized structural order and disorder.

Fullerene cages are known to undergo transformations under pressure, and

collapse into amorphous clusters when compressed at ambient temperature. In addition, the cages can arrange into stable lattices when solvated: the solvent molecules act as spacers between the ordered cages, and the resulting crystalline materials can be tuned by changing the fullerene species, their concentration, or the solvent. Wang and co-workers subjected one such crystalline material — C_{60} fullerenes solvated in *m*-xylene — to increasing pressures up to 60 GPa, and thoroughly characterized the changes it underwent by a variety of techniques.



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X-ray diffraction studies revealed that the long-range ordering of the material was retained at high pressures, and Raman spectroscopy gave evidence for the appearance of structural disorder in the fullerenes from about 32 GPa. The experimental data suggest that the cages collapse, first into hexagonal and pentagonal fragments, then into amorphous carbon clusters that feature a mixture of sp^2 - and sp^3 -hybridized atoms. The *m*-xylene molecules, however, were not affected under pressure and preserved the long-range periodicity of the lattice — indeed, subsequent solvent evaporation damaged the long-range order to yield an amorphous structure. These experimental observations are supported by molecular simulations, which also show the progressive deformation then collapse of the cages under increasing pressures.

This high-pressure approach seems a plausible route to synthesize a variety of crystalline phases from amorphous building blocks — not only from solvated fullerenes, but also more generally from systems containing deformable clusters and rigid linkers. AP

Written by Gavin Armstrong, Stuart Cantrill, Stephen Davey and Anne Pichon.

blogroll

Harder than flight

Why is discovering new drugs not as easy as designing passenger aircraft?

Do you remember how slow your computer was back in 1995 — that is, if you even had one? Remarkably, that was the year that the Boeing 777 entered the history books as the first aircraft designed solely using computers. Ash at The Curious Wavefunction has been pondering the reasons why, despite all the technical advances made recently and the huge impact they've had on other fields, computers have yet to make the design of even small-molecule drugs significantly easier. He muses, "we can routinely design airplanes, bridges and skyscrapers on a computer but are still light years behind when it comes to designing even 'simple' drugs" (<http://go.nature.com/MCBZ9E>). If that seems a little disheartening, let's not forget that it was only a little more than a century ago that the celebrated physicist Lord Kelvin declared heavier-than-air flying machines entirely impossible.

Meanwhile, lively debate between veteran medicinal chemist and blogger Derek Lowe and the authors of a recent paper in the *British Medical Journal* (<http://doi.org/h7k>) has dominated recent posts over at In The Pipeline (<http://go.nature.com/9n8aLN>). The topic: the 'innovation crisis' plaguing the pharmaceutical industry. Interestingly, it turns out that one of the authors in question is Professor Donald Light, a man who previously drew flak from Lowe over his co-authorship of a controversial 2011 paper that estimated the average R&D cost of a new drug at the rather low value of just over \$40 million (<http://go.nature.com/scFpcz>).

Finally, in somewhat contrasting posts, See Arr Oh, who blogs at Just Like Cooking, reflects on the tendency of studious chemists to work weekends (<http://go.nature.com/ESfzAK>), while Jess over at The Organic Solution discusses the chemistry behind a problem frequently faced by students: hangovers (<http://go.nature.com/ihqJj9>).

Written by BRSM, who blogs at <http://brsmblog.com/>