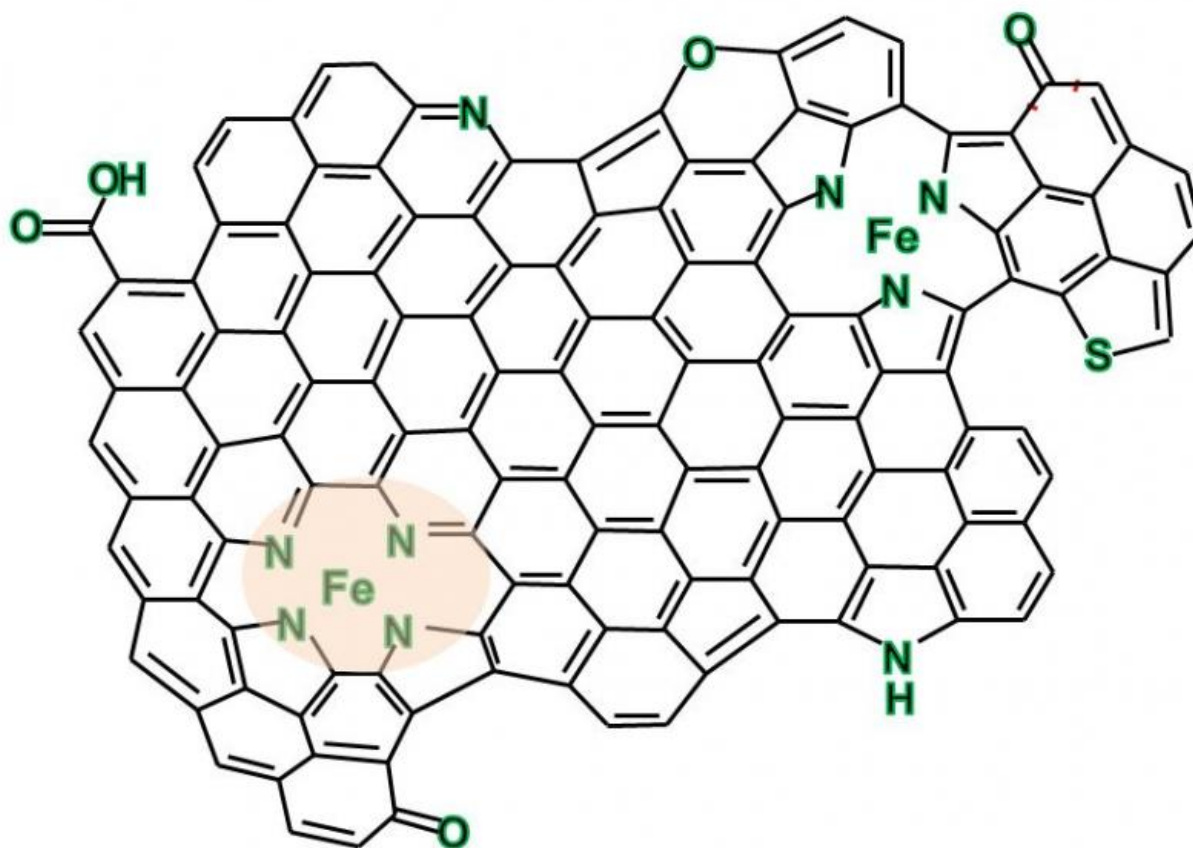


An alternative to platinum: Iron-nitrogen compounds as catalysts in graphene

January 27 2016



Nano-island of graphene in which iron-nitrogen complexes are embedded. The FeN₄ complexes (shown in orange) are catalytically active. Credit: S. Fiechter/HZB

Fuel cells convert the chemical energy stored in hydrogen (H_2) into electrical energy by electrochemically "combusting" hydrogen gas with oxygen (O_2) from the air into water (H_2O), thereby generating electricity. As a result, future electric automobiles might be operated quite well with fuel cells instead of with heavy batteries. But for "cold" combustion of hydrogen and oxygen to function well, the anode and cathode of the fuel cell must be coated with extremely active catalysts. The problem is that the platinum-based catalysts employed for this contribute about 25 per cent of the total fuel-cell costs.

However, iron-nitrogen complexes in graphene (known as Fe-N-C catalysts) have been achieving levels of activity comparable to Pt/C catalysts for several years already. "Systematic investigation of Fe-N-C catalysts was difficult though, since most approaches for preparing the materials lead to heterogeneous compounds. These contain various species of iron compounds such as iron carbides or nitrides besides the intended FeN₄ centres", explains Sebastian Fiechter of HZB.

High density of catalytically active centres

"We had already developed a new preparation method at HZB a few years ago to produce an inexpensive [catalyst](#) material from organometallic compounds such as iron or cobalt porphyrin", reports Peter Bogdanoff, HZB. Ulrike Kramm and Iris Herrmann-Geppert improved the process for producing it as part of their doctoral studies at HZB. As a result, the metal-N-C catalysts developed at HZB held the world record for the highest density of catalytically active centres of various nitro-metallic compounds up to about 2011. However, it remained unclear as to which inorganic compounds influenced the catalytic efficiency. The team was now able to determine this.

Purification process removes interfering compounds

The highlight in the current work is a purification process (a combination of thermal treatment with a subsequent etching step) by which the proportion of metallic compounds that interfere with catalytic activity can be substantially reduced, even for catalysts that are highly heterogeneous. The interesting thing here is that the activity increases enormously! Ulrike Kramm, who has since become a junior professor at TU Darmstadt, was successful in purifying several catalysts to such an extent that all the iron present in the graphene layers was exclusively in form of complexes made of iron and four nitrogen atoms (FeN₄). The scientists thereby disproved the hypothesis debated among experts by which improvement in the activity of the FeN₄ centres only resulted from promoters, as they are known, such as iron nanoparticles.

Now verified: FeN₄ centres provide the high catalytic efficiency even without promoters

"To check this hypothesis, we employed numerous complex measurement techniques like Mößbauer spectroscopy, electron paramagnetic resonance spectroscopy and X-ray absorption spectroscopy at BESSY II. These enabled us to precisely survey the atomic structure of the catalytic centres", Ulrike Kramm reports.

"The purification process enables us now to create catalysts having exclusively FeN₄ centres. This allows us to subsequently select compounds to be added afterwards as promoters that further improve the activity level or stability of these catalysts", as Ulrike Kramm summarises her research approach at TU Darmstadt.

Sebastian Fiechter and Peter Bogdanoff are continuing their research at HZB on novel catalysts, especially in regard to hydrogen generation using sunlight. "We can also use the insights into how these metal-N-C catalysts work in our on-going development of catalysing materials for

solar-based hydrogen production at HZB," says Fiechter.

Together, the research activities at HZB and TU Darmstadt could enable the development of a complete regenerative energy cycle, using solar hydrogen in low cost fuel cells, thus producing electricity without climate gas emission.

The results have now been published in the *Journal of the American Chemical Society*.

On an easy way to prepare Metal-Nitrogen doped carbon with exclusive presence of MeN₄-type sites active for the ORR, by Ulrike I. Kramm, Iris Herrmann-Geppert, Jan Behrends, Klaus Lips, Sebastian Fiechter and Peter Bogdanoff

More information: Ulrike I. Kramm et al. On an Easy Way To Prepare Metal–Nitrogen Doped Carbon with Exclusive Presence of MeN -type Sites Active for the ORR , *Journal of the American Chemical Society* (2016). [DOI: 10.1021/jacs.5b11015](https://doi.org/10.1021/jacs.5b11015)

Provided by Helmholtz Association of German Research Centres

Citation: An alternative to platinum: Iron-nitrogen compounds as catalysts in graphene (2016, January 27) retrieved 3 May 2024 from <https://phys.org/news/2016-01-alternative-platinum-iron-nitrogen-compounds-catalysts.html>

<p>This document is subject to copyright. Apart from any fair dealing for the purpose of private study or research, no part may be reproduced without the written permission. The content is provided for information purposes only.</p>
--