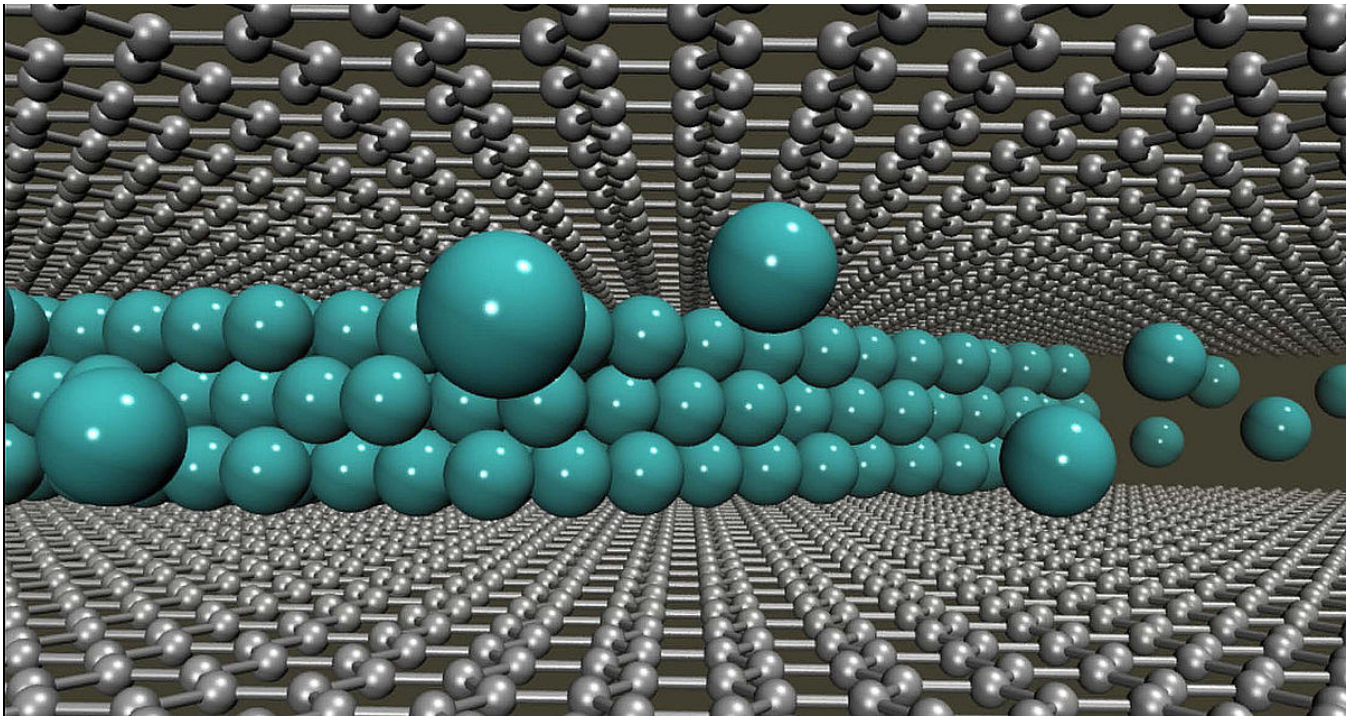


Figure 1: Model representation of a multilayered, densely packed storage of lithium between two graphene layers (Figure: Dr. M. Ghorbani-Asl / HZDR)

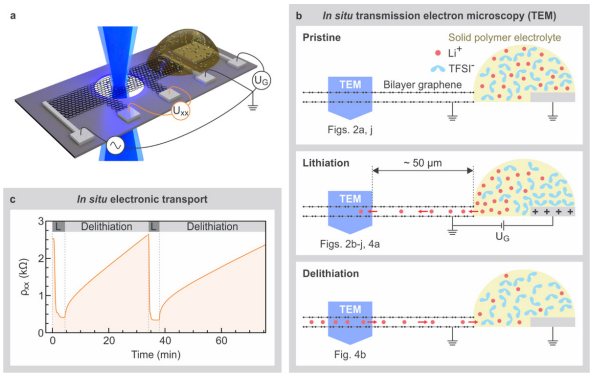
Lithium atoms on the move

SALVE provides sensational insights into miniature batteries

November 27th, 2018 - You can call it simply a sensation, what has been achieved by scientists from Stuttgart, Ulm and Dresden. Using the Sub-Angstrom Low-Voltage Electron microscope (SALVE), they were able to show in atomic resolution how lithium ions behave during electrochemical loading and unloading processes. They have demonstrated how the reversible lithium uptake occurs in a nanocell consisting of only one double layer of graphene. These highly relevant results for battery research were recently published in the scientific journal Nature.

„Pure carbon compounds are well suited for use in lithium-based electrochemical storage systems, where lithium is temporarily stored in the carbon host," explains Dr. Jurgen Smet, physicist at the Max-Planck-Institute for Solid State Research (MPI-FKF) Stuttgart. How it really looks, has studied in a joint project of Smet and the Ulm physicist Prof. Ute Kaiser. The aim of the research project funded by the Baden-Württemberg Foundation was to visualize and understand the storage and diffusion of lithium in two-dimensional carbon compounds such as graphene at the atomic level.

Smet and his PhD students Matthias Kühne and Sven Fecher have developed a „miniature battery" that is made up of a double layer of graphene. As a reminder: Graphene belongs to the so-called 2D materials and consists of a single layer of carbon atoms. At one end of the 0.3 nanometer thin, elongated electrochemical minicell, the scientists from Stuttgart put an electrolyte droplet containing a lithium salt. „To prevent any interference of the electrolyte with the electron microscopic image, it had to be precisely positioned and mechanically stabilized," Smet, head of the solid-state nanophysics research group at the MPI-FKF, explains. Therefore, the Stuttgart group needed a trick: added polymers that cure under UV light, transform the drop to a gel-like solid, which remains where it is. If a voltage is now applied to the nanocell, the lithium ions migrate from the electrolyte droplet into the interspace between the graphene double layer and accumulate there (intercalation). When the potential difference is removed, the stored lithium accumulation dissolves and the lithium migrates back into the electrolyte drop.

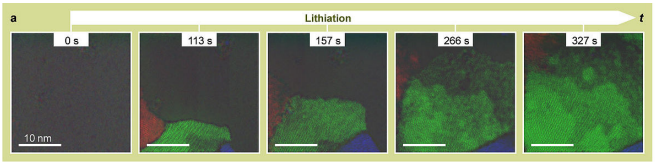


A graphene bilayer lies over a hole of a carrier substrate. At one end of the carrier, an electrolyte drop is applied by dissolving lithium salt. By applying a voltage, the lithium begins to intercalate between the graphene layers. If the voltage disappears, the lithium migrates back into the electrolyte (picture: Matthias Kühne, Dr. Jurgen Smet / MPI-FKF)

The surprise: In the nanocell of graphene, the lithium accumulates several layers

But in what form is the lithium stored? What form does

the process of intercalation take? At the atomic level, such processes are very difficult to observe „in situ“ - i.e. „live“. Using the supermicroscope SALVE the team at Ulm University led by Kaiser has been able to demonstrate this for the first time ever. „The result surprised us a lot: In contrast to conventional graphite-based battery cells, where only a few, tightly packed lithium layers are sandwiched between two carbon layers, several very densely packed lithium layers were found here“, Dr. Felix Börrnert and Dr. Johannes Biskupek, member of the Department of Materials Science for Electron Microscopy at the University of Ulm explain. The loading and unloading experiments with the „miniature battery“ on the SALVE microscope were repeatedly and repeatedly reproduced over many weeks. In addition, it had to be ensured that the TEM images are really showing lithium. For this purpose, the elemental composition of the observed structures was chemically investigated using the electron energy loss spectrometer belonging to the SALVE microscope.

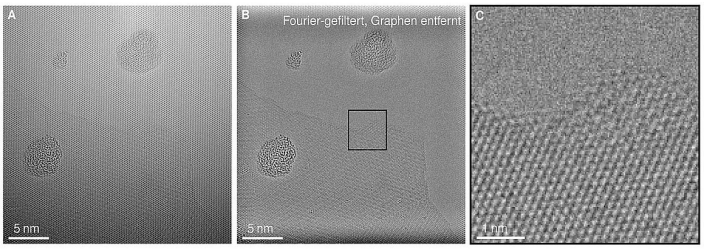


Li crystal growth between a graphene bilayer as a function of the loading time with lithium. The different colors show different crystal orientations of the stored lithium (photograph: Dr. Felix Börrnert / Uni Ulm)

SALVE provides unique insights into the nanocell

„It is an enormous scientific challenge to make the diffusion of such a light element as lithium in a ‚graphene sandwich‘ electron microscopically visible“ says Kaiser. The TEM images are either too low in contrast, or there is massive damage to the materials due to the electron beam. „With SALVE and thanks to a trick - we have been able to calculate the regular lattice structure of the graphene bilayer from the electron microscope image, we master both challenges„ said Kaiser. The spherical- and chromatic aberration-corrected low-voltage transmission electron microscope allows high-resolution and high-contrast images at a sub-atomic resolution of 75 picometres at a voltage of 80 kV. This voltage is comparatively low and therefore also allows the investigation of sensitive 2D materials such as graphene. The device was developed as part of the multi-year research initiative „Sub-Ångstrøm Low-Voltage Electron Microscopy“ (SALVE) at the University of Ulm.

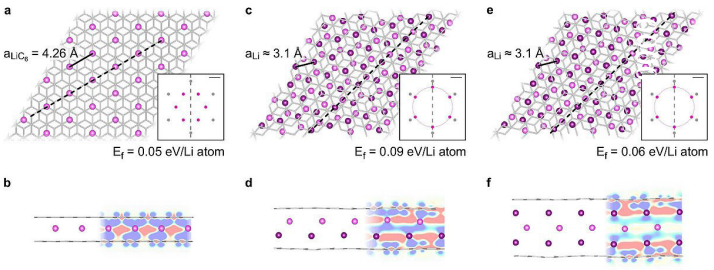
For the „in situ“ experiments of the reversible lithium deposition in the nanocell, the researchers from Ulm and Stuttgart worked together for many weeks on the SALVE microscope. The scientists were particularly fascinated by the knowledge of how perfectly the microscopic images fit the theoretically postulated configurations that the colleagues from Dresden calculated. Based on so-called density-functional-theory-calculations, the physicists Dr. Mahdi Ghorbani-Asl and Dr. Arkady Krasheninnikov at the Helmholtz-Zentrum Dresden-Rossendorf (HZDR) showed that the formation of multilayer lithium deposits is likely in good agreement with the observations „Ultimately, what determines the likelihood of a particular structure is how stable that particular phase is in certain circumstances,“ explains Krasheninnikov.



TEM image during loading of lithium into the graphene bilayers. A) original image, B) The graphene bilayer was optically removed from the image by a special filter, C) enlarged detail from the filtered image (photo: Dr. Felix Börrnert / Uni Ulm)

Basic insights for battery research

The research project was supported by the Baden-Württemberg Stiftung. The work is also embedded in the „Graphene Flagship“ initiative of the European Union as well as from Ulm in the new cluster of excellence for battery research. „The results of this research project are of fundamental importance for battery research, as they provide insights into the course of elementary processes in electrochemical energy storage,“ Smet and Kaiser agree. And who knows, maybe the new insights will inspire the design of future carbon based storage systems.



The figure shows the result of density-functional-theory calculations of lithium between graphene layers at different loading densities. The atomic structure and the electrical charge transfer are shown graphically (Figure: Dr. M. Ghorbani-Asl / HZDR)

FOCUS

Original publication:

(1) Matthias Kühne, Felix Börrnert, Sven Fecher, Mahdi Ghorbani-Asl, Johannes Biskupek, Dominik Samuelis, Arkady V. Krasheninnikov, Ute Kaiser & Jurgen H. Smet: Reversible superdense ordering of lithium between two graphene sheets. In: Nature, published online: 26 November 2018 doi 10.1038/s41586-018-0754-2

Press article published by idw-online.de / focus.de / labo.de / git-labor.de / arstechnica.com ... (in German)